Universidade de Aveiro Departamento de Ambiente e Ordenamento
2008

Joana Lapão Rocha

Capacidade de absorção de uma suspensão aditivada de pedra calcaria

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia do Ambiente realizada sob a orientação científica do professor Luís António da Cruz Tarelho, Professor Auxiliar do Departamento de Ambiente e Ordenamento da Universidade de Aveiro.

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palavras-chave

Dessufurização de efluentes gasosos, dióxido de enxofre, pedra calcária, absorção.

resumo

Este trabalho apresenta os resultados das pesquisas relativas à capacidade de absorção de suspensões de calcário aditivado, com base na revisão de literatura e da aplicação de modelos matemáticos específicos.

Neste trabalho estão resumidas informações sobre a evolução histórica das emissões de enxofre na República Checa assim como também uma abordagem global. São apresentadas as legislativas validas relativas as emissões de dióxido de enxofre.

Além disso, com base na pesquisa teórica são apresentadas informações sobre as tecnologias disponíveis e utilizadas para reduzir o conteúdo de enxofre nas emissões.
São mostradas tecnologias primárias de dessulfurização (por dessulfurização de carvão ou gás energético), bem como tecnologias secundárias de dessulfurização do gás de combustão.
Para o processo húmido de dessulfurização (usando calcário) é dedicado um capítulo separado devido a extensiva informação recolhida que incluem (excepto caracterização de aparelhos tecnológicos) informações sobre o processo e parâmetros já feito sobre as experiências com aditivos.
Na parte experimental é descrita o método usado no laboratório para avaliar a eficiência de remoção de dióxido de enxofre, por suspensões calcárias com diferentes concentrações de aditivos com um reactor em regime descontínuo.
É dedicada atenção a uma série de aditivos especialmente os orgânicos (di) ácidos com o objectivo de concluir qual a sua influência e adequação ao uso industrial.
Os dados medidos foram avaliados e organizados em tabelas e gráficos que, em detalhe, se discutiu a comparação dos resultados obtidos para cada parâmetro.
O conjunto de dados recolhidos em laboratório espera se serem capazes de ajudar no problema de dessulfurizacao húmida dos gases de combustão.

keywords Wet flue gas desulphurization, sulphur dioxide, limestone, absorption, organic acids

abstract

This work presents the results of research concerning the absorption ability of additived limestone suspension, based on the literature review and the application of specific mathematical models.

In this work is summarized information about historical development of sulphur emissions in Czech Republic as in a global approach.
Here is adumbrated the valid legislative concerning sulphur dioxide emissions. Further, is in the form of summarized literary background research, and information about available technologies used for reducing the sulphur emissions. Here are shown “prime” technologies (for desulphurization of coal or energetic gas) as well as “secondary” technologies desulphurization of combustion gas.
For wet flue gas desulphurization (using limestone) is devoted a separated chapter due to its extensiveness that include (except characterization of technological apparatus) available information about the process parameters and about already done experiments with additives.
In the experimental part is described the sample base and the built-up laboratory device for measurement of “breakthrough curves of SO_2 of absorptive suspension on batch reactor.
The attention is devoted to the series of additives specially the organic (di)acids with the aim to pass judgment on its influence and fitness to industrial use.
The measured data was first evaluated and than well-arranged graphs and tables, in detail, discussed by comparison of results for every parameter.
Data collection obtained on the laboratory work is able to help on the problem of wet flue gas desulphurization method.

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Acronyms

S_m	Specific sulphur content	[g.MJ^{-1}]
S^d	Specific sulphur content in dry state	[% wt]
S^r	Sulphur content in original state	[% wt]
W_t^r	Water content in original state	[% wt.]
Q_i^r	Heat value of the fuel in its original state	[MJ.kg^{-1}]
V_g	Settling speed	[m.s^{-1}]
W	Wet deposition	-
L/G	Ratio between scrubbing liquid flow and gas flow	-
μ	Oversaturation degree	-
A	Activity ions	-
K	Product solubility	-
[$CaCO_3$]	Calcium carbonate concentration	[mol.dm^{-3}]
[H^+]	Concentration of hydrogen ion	[mol.dm^{-3}]
S_{sp}	Specific surface area	[m^2.g]
K_a	Dissociation constant	-
EDTA	ethylenediaminetetraacetic acid	-
BET	Surface adsorption modelof solid substances Brunauerem, Emmetem Tellerem	-
$\dot{V}^0$	Gas flow	[m^3/s]
V_r	Reaction volume	[m^3]
τ	Time	[s]
y_i^0	Entering SO_2 concentration on gas phase (g)	[mol/m^3]
y_i	SO_2 concentration on gas phase (g)	[mol/m^3]
x_i	SO_2 concentration on liquid phase (l)	[mol/m^3]
N	Order of reaction	-
$C_{SO_2}[mg.m^{-3}]$	SO_2 concentration	[mg.m^{-3}]
$C_{SO_2}[ppm]$	SO_2 concentration	[ppm]
$M_{SO_2}[g.mol^{-1}]$	SO_2 molecular mass	[g.mol^{-1}]
η_{des}	Desulphurization efficiency	[%]
C_0	Inlet concentration	[mg.m^{-3}]
C_1	Outlet concentration	[mg.m^{-3}]
FGD	Flue gas desulphurization	

WFGD	Wet flue gas desulphurization
EEA-32	32 member countries of the EEA (EU-15 + EU-10 + EFTA-4 + Romania , Bulgaria and Turkey)

1 Introduction

Throughout the history of humankind, changing lifestyles, the need to improve the quality of life and encourage economic progress have been accompanied by a growing need for energy.

Usually, the need for energy requires means of combustion which, in turn, result in the release of substances into atmosphere, which affect the environment negatively. Until the ideal clean energy/technology is found, current solutions need to be improved.

Today, wet flue gas desulphurization has a dominant role in the desulphurization processes, in the thermal power plants that use coal as their energy source, releasing sulphur oxides from the burning chamber. The main advantage of wet flue gas desulphurization over other desulphurization combustion technologies is especially the high efficiency throughout the process. This technology is capable of reaching the increasing stringent emission limits, allowing it to consolidate its position as the most popular technology in the world, in this area, although high efficiency can mean high investment and operating costs. Increasing the efficiency of this method, leading to a decrease the investment and operating costs (designing a new facility) or extending the lifetime of the older equipment (which is no longer capable of reaching the stringent emission limits), it is certainly, at least from a financial perspective, an idea worth exploring.

One way of increasing the efficiency of the wet flue gas desulphurization method lies in the application of additives into the limestone suspension. Additives can be divided into two categories: organic and inorganic, depending on their chemical structure. The inorganic additives used are salts, mostly magnesium. The disadvantage of these additives is their sensitivity to ions Cl^- and F^- ion the flue gas. When these additives are used, it is necessary to guarantee the removal of the chloride and fluoride before the absorption, given that they can react, hence closing the porous surface of limestone, by forming aluminium chloride and aluminium fluoride.

This work focuses on the wet flue gas desulphurization with the application of organic acids.

2 Theoretical Framework

The problem of SO_2 emissions started in the 70s, during the 20th century. The first desulphurization technology was installed in Japan and in the USA, later being implemented in other countries.

Considering that in the Czech Republic energy requirements are catered for through the burning of coal, mostly brown coal (with a high sulphur content), environmental concerns led to the implementation of desulphurization systems in the power plants.

In this section, the information analysed is summarized regarding sulphur dioxide emissions, the legislative provisions for the reduction of sulphur dioxide emissions in the Czech Republic are presented together with a discussion about the evolution of desulphurization technologies throughout time.

2.1 Legislation in the Czech Republic for the protection of air quality

2.1.1 Existing provisions

Currently, in the Czech Republic, the validity of the Clean Air Act No. 472/2005 Coll. [22], superseded the original and amended Law No. 86/2002 Coll. [23], which reflects new concerns which come through the changes made by Act No. 521/2002 Coll. Law No. 92/2004 Coll. Act No. 186/2004 Coll. Act No. 695/2004 Coll. Act No. 180/2005 Coll., And Act No. 385/2005 Coll. This law establishes:

• rights and obligations of persons and administrative offices for the protection of ambient air before the emission of pollutants due to human activity, also covering the requirements concerning the handling of controlled substances that deplete the ozone layer and of products containing such substances;

• conditions for further reduction of discharged pollutant quantities that cause an adverse effect on life, on human and animal health, and on the environment.

The main objective of this Act is to ensure the full compatibility of the environmental law in the Czech Republic with EU legislation and, simultaneously, create the conditions for the fulfilment of the requirements imposed on the Czech Republic in the light of international commitments which the Czech Republic aims at complying with, which deal with the protection of the atmosphere, the ozone layer and the climate of the Czech Republic.

This law included detailed rules: [21]

• 350/2002 Coll. Establishing the values and procedures of monitoring, assessment, evaluation and management of air quality.

• 351/2002 Coll. Establishing binding emission ceilings for certain atmospheric pollutants and the method of preparation and realization of emission inventories and emission projections.

• 352/2002 Coll. Establishing emission limits and other operation conditions for the combustion of stationary sources of air pollution.

• 353/2002 Coll. Establishing emission limits and other operation conditions of other stationary sources of air pollution.

• 354/2002 Coll. Establishing emission limits and other conditions for the incineration of waste.

• 355/2002 Coll. Establishing emission limits and other operation conditions for other stationary sources of air pollution-emitting volatile organic compounds (VOC) from the process of applying organic solvents to the storage and distribution of petrol.

• 356/2002 Coll. Establishing the list of pollutants, general emission limits, transmission of news and information, surveying the percentage of pollutants discharged, the darkness of smoke, permissible odour extent and intensity of odours, the conditions for the obtention of authorization permits and licences, definition of requirements for the management of operational records concerning sources of air pollution and the conditions for their implementation.

• 357/2002 Coll. Laying down the requirements for the quality of fuels regarding the protection of air quality.

• 358/2002 Coll. Laying down conditions for the protection of the ozone layer.

2.1.2 Sulphur dioxide emission limits

In the conditions mentioned above, the emission limits for sulphur dioxide combustion of solid, liquid and gaseous fuels are defined. [21,22]

2.1.3 Emission limits for solid fuels

A) For each facility, the existing resources are valid under Section 2 point. g) The following SO_2 emission limits are expressed in [$mg.m^{-3}$] (with an oxygen content of 6%), under normal conditions and dry gas.

Table 1 - Sulphur dioxide emission limits.

Thermal capacity	Up to 50 MW [$mg.m^{-3}$]	50-300 MW [$mg.m^{-3}$]	>300 MW [$mg.m^{-3}$]
Fluidize furnace	800	500	500
Other kinds of furnace *)	2500	1700	500

*) also for grade combustion chambers and chambers with external fluidize reactor

Note:

1st) These emission limits are applied to the existing facilities of resources, issued in the original building permit, before the 1st of July of 1987, and applies to the thermal performance of single facilities.

2nd) From the 1st of January of 2008, the resources have had to meet the emission reduction plan requirements. The plan sets emission ceilings to protect the air, which are based on limits set out under the letter B. The emission limits for each facility, which was issued in the building permit after the 1st of July of 1987, applies to all thermal power resources.

B) The emission limits for new sources, with building permits issued from the 1st of July of 1987 to the 31st of December of 2002, pursuant to Section 2, point h) expressed [$mg.m^{-3}$] (with an oxygen content of 6%) under normal conditions and dry gas.

Table 2 - Sulphur dioxide emission limits for solid fuels.

Thermal capacity	50-100 MW [$mg.m^{-3}$]	100-500 MW [$mg.m^{-3}$]	>500 MW [$mg.m^{-3}$]
Limit	2000	2000 to 400	400

C) The emission limit values for new future resources, with building permits issued after the 1st of January of 2003, under Section 2 point. j) expressed [$mg.m^{-3}$] (the oxygen content of 6%) under normal conditions and dry gas.

Table 3 - Sulphur dioxide emission limits for new future solid fuels.

Type of fuel	50-100 MW [$mg.m^{-3}$]	100-300 MW [$mg.m^{-3}$]	>300 MW [$mg.m^{-3}$]
Biomass	200	200	200
Other solid fuels	850	200	200

2.1.4 Emission limits for liquid fuels

A) In order to guarantee that emission values are below the limit value using the existing resources under Section 2 point g) expressed [$mg.m^{-3}$] (the oxygen content of 3%) under normal conditions and dry gas.

Table 4 - Sulphur dioxide emission limits for liquid fuels.

Thermal capacity	to 50 MW [$mg.m^{-3}$]	50-300 MW [$mg.m^{-3}$]	>300 MW [$mg.m^{-3}$]
Limit	(not specified)	1700	500

Note:

1st) These emission limits apply to the facilities of existing resources, which were issued in the original building permit before the 1st of July of 1987, and applies to the thermal performance of single facilities.

2nd) From the 1st of January of 2008, thermal power plants will have the resources to meet emission reduction plan. The plan establishes emission ceilings to protect the air, which are based on limits set out under the letter B. The emission limits for each facility, with building permits issued after the 1st of July of 1987, with respect to thermal capacity of entire resources, will have emission limits determined according to the plants' capacity.

B) The emission limits for new sources, for which building permits were issued from the 1st of July of 1987 to the 31st of December of 2002, pursuant to Section 2, point. h) expressed [$mg.m^{-3}$] (the oxygen content of 3%) under normal conditions and dry gas.

Table 5 - Sulphur dioxide emission limits for new liquid fuels.

Thermal power	50-300 MW [mg.m^{-3}]	300-500 MW [mg.m^{-3}]	>500 MW [mg.m^{-3}]
Limit	1700	1700 to 400	400

C) The emission limit values for new future resources, with building permits issued after the 1st of January of 2003, under Section 2 point j) expressed [mg.m^{-3}] (the oxygen content of 3%) under normal conditions and dry gas.

Table 6 - Sulphur dioxide emission limits for new future liquid fuels. [21]

Thermal power	50-100 MW [mg.m^{-3}]	100-300 MW [mg.m^{-3}]	>300 MW [mg.m^{-3}]
Limit	850	400 to 200	200

2.1.5 Emission limits for gas-fired sources

A) For each facility with resources under Section 2 point g) expressed [mg.m^{-3}] (the oxygen content of 3%) at normal conditions for dry gas.

Table 7 - Sulphur dioxide emission limits for existing resources for gaseous fuels. [21]

Fuel	Limit [mg.m^{-3}]
Gaseous fuels from public distribution networks	35
Gaseous fuels fuel from outside the public distribution networks, and coke* oven gas	900
Liquefied gas	(not set)

* by product from high temperature black coal carbonization process

Note:

1st) These emission limits apply to the facilities of existing resources, with the original building permit issued before the 1st of July of 1987, and applies to the thermal capacity of single facilities.

2nd) From the 1st January of 2008, the resources have to meet the emission reduction plan. The plan sets the emissions ceilings to protect the air, which are based on limits set out under the letter B. The emission limits for each facility, with building permits issued after the 1st of July of 1987, applies to all power resources

B) The emission limits for new sources, with building permits issued from the 1st of July of 1987 to the 31st of December of 2002, according to Section 2, point. h) expressed [$mg.m^{-3}$] (the oxygen content of 3%) on a normal state conditions and dry gas.

Table 8 - Sulphur dioxide emission limits for gas fired sources. [21]

Fuel	Limit [$mg.m^{-3}$]
Gaseous fuels in general	35
Liquefied gas	5
Low heat value gases from gasification or by products from refining, coke oven gas, blast furnace gas, converter gas	800
Gas from coal gasification	(not set)

C) The emission limit values for new future resources, with building permits issued after the 1st of January of 2003 under Section 2 point. j) expressed [$mg.m^{-3}$] (the oxygen content of 3%) under normal conditions and dry gas.

Table 9 - Sulphur dioxide emission limits for new gas fired sources. [21]

Fuel	Limit [$mg.m^{-3}$]
Gaseous fuels in general	35
Liquefied gas	5
Coke oven gas	400
Blast furnace gas, converter gas*	200

* by product from iron industry

2.2 Categorization of sources of air pollution

Sources of pollution are divided according to their heat capacity and relevance of air pollution control: [22]

• Greatest sources - sources of rated heat capacity input of 50 MW and above, without taking into account the nominal heat power.

• Great sources - technological facilities containing stationary fuel-burning equipment with a rated thermal output performance from 5 MW to 50 MW.

• Median sources - technological facilities containing stationary equipment to burn fuel with a thermal output capacity from 0,2 MW to 5 MW.

• Small sources - technological devices containing stationary equipment to burn fuel with a thermal output capacity of less than 0,2 MW.

• Mobile sources - mobile equipment vehicles, portable devices equipped with internal combustion engines, which emit pollutants into the air, especially road motor vehicles, railway vehicles, ships and aircrafts.

• Stationary sources - devices for burning fuel or other technological device, which emits pollutants into the air.

2.3 Sulphur dioxide

Considering that sulphur is a necessary component of biological systems, sulphur is ubiquitous in the biosphere. As a result, sulphur often occurs in relatively high concentrations in fossil fuels, with coal and crude oils deposits commonly containing 1-5% sulphur according to weight. The widespread combustion of fossil fuels has, therefore, greatly increased sulphur emissions into the atmosphere, with an anthropogenic component substantially higher than the natural emissions on a global basis. Anthropogenic emissions have increased sulphur deposition and atmospheric sulphate loadings in many areas. Early studies, which focus on these problems, have analysed the impact of these substances on ecosystems and human health, which occur on both local and regional scales. Sulphate acid deposition can be detrimental to ecosystems, harming aquatic fauna and flora, as well as having a negative impact on a wide range of terrestrial plant life. In addition, aerosols particles have adverse effects on human health, especially in the form of respiratory elements, as well as the tetragenic effects which have been identified. Sulphur dioxide forms sulphate aerosols that are thought to have a significant effect on global and regional climates. Sulphate aerosols reflect sunlight into space and also act as cloud condensation nuclei, which tend to make clouds more reflective and change their lifetimes.

Sulphur dioxide is among the most harmful pollutants emitted into the atmosphere, both due to its quantity, and due to its harmful effects in general. It is a colourless, slightly poisonous liquefiable gas, with a sweet taste and a specific odour. The melting point is at -72,5℃ and boiling point at -10ºC. The multifaceted impacts of sulphur dioxide emissions motivates a closer examination of possible future paths for future regional and global emissions.

2.3.1 Sources of sulphur dioxide

Sulphur (S) is present in fossil fuels, such as oil and coal, and is oxidised during combustion, forming sulphur dioxide (SO_2).

Nearly all the sulphur dioxide emitted into the atmosphere is created by the combustion of substances that are present in nature, and which contain sulphur whether in its elementary form, or as a component of ore, or fossil fuel. The fossil fuel can be coal, oil and/or natural gas. The ores are particularly sulphuric ore such as pyrites, sphalerite (zinc blend) and cinnabar (mercury sulphide). Therefore, the emissions occur primarily through the production of steam and electricity, through the metallurgical processing of ores, petroleum refining and through the production of sulphuric acid.

Sulphur present in coal is represented in two different forms:

• organic;

• inorganic. The inorganic can be further broken down into:

- pyrite FeS_2
- sulphates SO_4^{2-}
- sulphides S^{2-} (chemically coupled)
- the elemental S

Each of these forms behaves differently with regard to their chemical and physical processes. Pyrite has its organic chemical conversion subjected to a temperature below 1000℃ and, through combustion, is transformed into a gaseous SO_2, while sulphate remains unchanged in the form of solid residue (ash). Temperatures around 1500℃ lead to a complete breakdown of sulphate. [33, 34] The rate of emissions of sulphur oxides released by the combustion of fuel is considered to be a specific content of S, which is defined as the weight of sulphur content in coal [g] relative to [1 MJ] calorific value of fuel: [34]

$$S_m = \frac{S^r * 10}{Q_i^r} \qquad (1) \qquad\qquad S^r = S^d * \frac{100 - W_t^r}{100} \qquad (2)$$

By merging the two terms, the following is obtained:

$$S_m = \frac{S^d * \left(100 - W_t^r\right)}{10 * Q_i^r} \qquad (3)$$

S_m - Specific content of S [g.MJ^{-1}]

S^d - Sulphur content in dry state [% wt]

S^r - Sulphur content in original state [% wt]

W_t^r - Water content in original state [% wt]

Q_i^r - Heat value of the fuel in its original state [MJ.kg^{-1}]

The Czech brown energetic coal has a low calorific value and a relatively high sulphur percentage if compared to black energetic coal imported into Western Europe, from China or South Africa, which has a higher calorific value and a lower sulphur content.

Table 10 - Comparison of specific sulphur content in black and brown coal. [34]

Parameter	Black coal used in Western Europe	Brown coal used in the Czech Republic
Heating value	cca 25 MJ.kg^{-1}	cca 9 – 12 MJ.kg^{-1}
Sulphur content	0,5 – 0,8 % wt.	1,3 % wt
Specific sulphur content with respect to heat value	0,2 – 0,3 g S.MJ^{-1}	1,1 – 1,5 g S.MJ^{-1}

2.3.2 Impact of sulphur dioxide on the environment

After the emission of sulphur dioxide into the atmosphere, the substance is not permanently accumulated; it is removed from the atmosphere through two processes: dry deposition and wet deposition.

Dry deposition implies the contact of particles and gases into the Earth's surface and sea without the intervention of atmospheric water (rain, snow, fog) [9]. The effectiveness of dry deposition can be expressed as “settling speed Vg”.

$$V_g[m.s^{-1}] = \frac{stream\ of\ SO_2\ \ [\mu g.m^{-2}.s^{-1}]}{Atmospheric\ concentration\ \ [\mu g.m^{-3}]} \qquad (4)$$

Table 11 – Typical deposition speed. [9]

The surface on which SO_2 falls	Deposition speed [cm.s^{-1}]
Field (green surface)	1,0
Ocean	0,5
Soil	0,7
Forest	2,0

Wet deposition is the removal of pollutants by rainfall and includes both the conversion of pollutants in the presence of water (into a layer of clouds), and their subsequent removal by rainfall.

The overall effectiveness of wet deposition can be expressed by "W", sometimes wrongly called "washing factor".

$$W = \frac{SO_2\ Concentration\ in\ precipitation\ \ [mg.kg^{-1}]}{SO_2\ Concentration\ in\ air\ \ [mg.kg^{-1}]} \quad (5)$$

The typical removal ratio for sulphate ion is the value of 700. [9]

In the presence of water drops (fog, aerosols), but also in the gaseous phase, sulphur dioxide is oxidised into sulphuric acid, which is one of the most important components of what is commonly known as acid rain. Sulphuric acid, as well as sulphate, leads to photochemical oxidation, particularly in the presence of nitrogen oxides. The direct rainfall removes approximately 80% of sulphur dioxide from the atmosphere. Gaseous SO_2 is very quickly absorbed by plants and by the soil surface. Overall, an estimated residence time of SO_2 in the air is of around 2-7 days. [4]

Sulphur dioxide is oxidised by the hydroxyl radical in the presence of other molecules (the third body) in the gaseous phase as illustrated by the following equations:

$$^{\bullet}OH(g) + SO_2(g) + M \rightarrow HSO_3^{\bullet}(g) + M \quad (6)$$

$$HSO_3^{\bullet}(g) + O_2(g) \rightarrow HO_2^{\bullet}(g) + SO_3(g) \quad (7)$$

$$SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g) \quad (8)$$

Due to low volatility, sulphuric acid condensates on the surface of droplets or particles. Faster oxidation of SO_2 occurs in the liquid phase

$$SO_2(g) \leftrightarrow SO_2(aq) \quad (9)$$

$$SO_2(aq) + H_2O(aq) \leftrightarrow H_2SO_3 \leftrightarrow H^+ + HSO_3^- \leftrightarrow 2H^+ + SO_3^{2-} \quad (10)$$

$$HSO_3^- + H_2O_2(aq) + H^+ \rightarrow SO_4^{2-} + H_2O(aq) + 2H^+ \quad (11)$$

$$SO_3^{2-} + O_3(aq) \rightarrow SO_4^{2-} + O_2(aq) \quad (12)$$

The last reaction (12) takes place at pH greater than 6, which occurs only in cloud drops containing basic substances such as ammonium or sodium ion.

Oxidation of SO_2 to SO_4^{2-} in clouds, and cloud water fog, is usually much faster than homogeneous oxidation of SO_2 in the gaseous phase generated by hydroxyl radical. The speed of oxidation in the gaseous phase is from 0.5 to 1%.h^{-1}, but the speed of oxidation in the liquid phase of rainwater can reach percentages that vary from 10% to 50%.h^{-1}. An important process, mainly in the case of pollution in cities and in industrial areas, is a fast heterogeneous catalytic oxidation of SO_2 in the wet aerosol particles. An example is the oxidation of SO_2 in the looping smoke stack from coal-fired power plants to ash particles, containing, for example, trivalent iron or diatomic manganese (catalysts). [10]

While natural rain has a pH of 5.0 to 5.6 (affected only by the concentration of CO_2 in the air), the pH of acid rain (or fog) ranges from 2.0 to 5.6.

One of the earliest harmful effects of sulphur dioxide identified is the damage of forests and other plant life, which has been known for over one hundred years. In an accidental exposure to concentrations of SO_2 about 1 mg.m^{-3}, within only a few hours, leads to acute damage to leafy surfaces, which is attributed to the direct influence of SO_2 redox characteristics, reflected by the collapse of tissues and their subsequent death. The predominant impairment is chronic exposure to SO_2, which leads to the accumulation of sulphate in the tissue, and possibly decreasing the pH to reduce the H_2S. The result is a synthesis of chlorophyll inhibition, expressed by the loss of green leaves and restrictions on photosynthesis causing the trees and plants' death. Conifers are particularly resistant to sulphur effects because the needles only changed every three years, so they accumulate the annual sulphate which has fallen. [4]

Sulphur dioxide is soluble in water, so, it is easily captured on the surface of nasal mucous and upper respiratory tract mucous membranes. Being exposed to high concentrations of SO_2 and H_2SO_4, leads to respiratory problems such as bronchitis. SO_2 is absorbed into the upper respiratory system tract in percentages which vary between 95% and 98%. Sulphur dioxide causes a reduction of vital lung capacity and reduces the production of red blood cells, leading to anaemia. Persistent exposure to concentrations of 0.15 mg.m^{-3} leads to chronic respiratory tract diseases, which, with accidental exposures to conditions with air concentrations of SO_2 above 1 mg.m^{-3}, lead to increased mortality rates. [4,9]

Living in an environment which is permanently polluted by sulphur dioxide has resulted in increased morbidity and mortality in the population, degradation of forests, plant, animal

and agricultural production. Besides these effects on human health and on the environment, sulphur dioxide reacts in to the water present in the air, forming sulphuric acid which destroys practically all types of building materials.

2.3.3 Evolution of sulphur dioxide emissions

2.3.3.1 Global emissions of sulphur

Figure 1 illustrates the evolution of global and regional emissions of sulphur in the period comprehended between the years 1850 to 2000. The maximum emissions were achieved in 1989, with 74 100 Gg

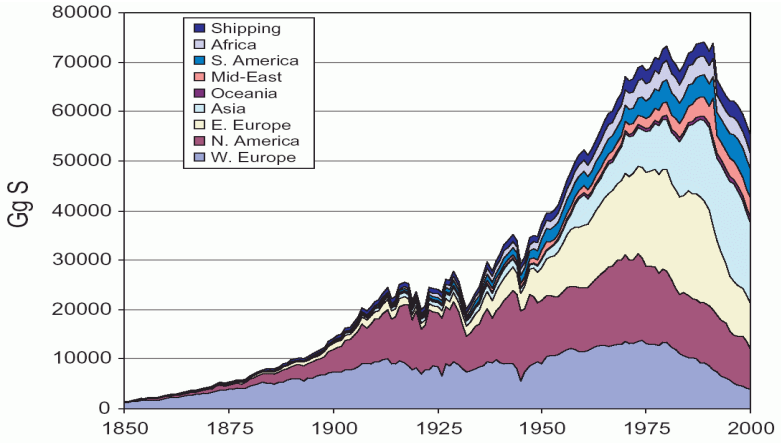

Figure 1 - Global and regional sulphur emissions in the period between 1850 to 2000. [29]

In 1980, the global emissions of sulphur reached 73 200 Gg, and then started to decline as a result of the reduction of emissions in Western Europe and North America. Re-growth in the percentage of emissions in the second half of the 80s, in the twentieth century, was caused by growing emissions in Asia. Subsequent steep decline, broken only by oil fires in Kuwait (which contributed with approximately 4 700 Gg), is mainly a result of the economic collapse of Eastern European countries and of the Soviet Union. [29] The other figure reveals visible variations in the emissions of sulphur in the various regions in the 80s and 90s of the 20th century.

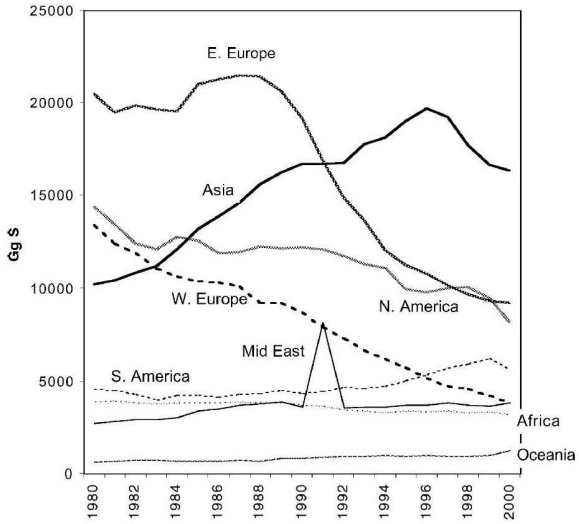

Figure 2 - Regional sulphur emission trends between the 80s and 90s of the 20th century.[29]

Distribution of SO_2 emissions in 2005, in the countries of the European Union, according to different sources presented in Figure 3, reveal a dominant sharing of electricity production.

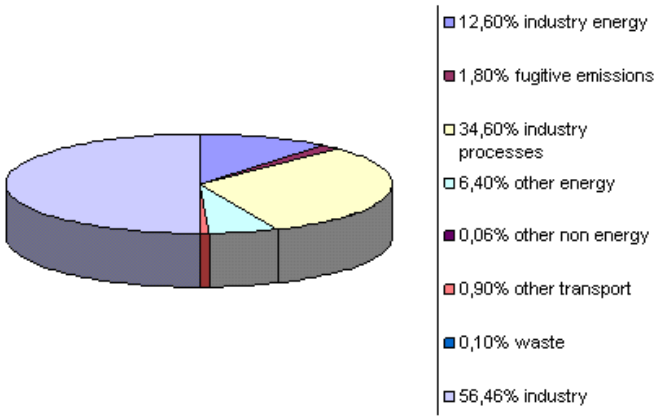

Figure 3 - Sulphur dioxide emissions in the countries of the EEA-32.

The changes in the sulphur dioxide emissions in each sector from 1990 to 2005 are presented on figure 4.

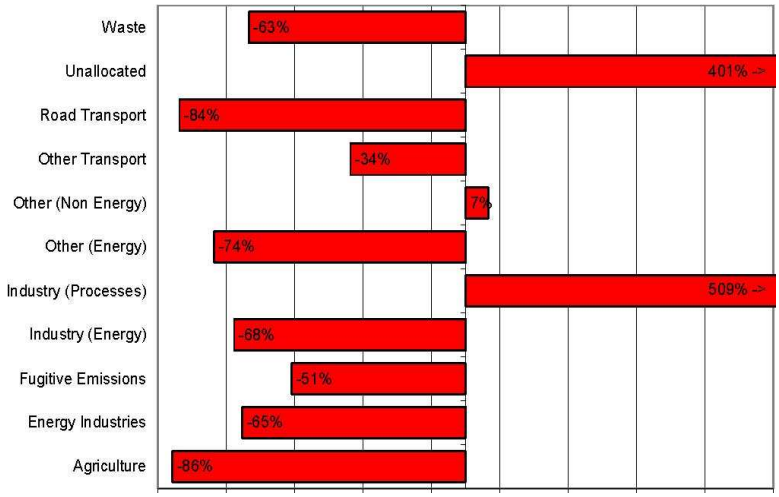

Figure 4 - Change (%) in the sulphur dioxide emissions in each sector from 1990 to 2005 for EEA-32.

The proposal for the development of SO_2 emissions in the future and the projected scenario shown in Figure 5 concerning global emissions of SO_2 reveal that these will be increasingly influenced by developing countries, particularly Asia. The emissions in these countries are growing mainly due to an increase in the use of coal (particularly due to increasing electricity consumption) and a growth in the population. In most industrialised countries (full line curves) emissions will decrease (see table 12). The decline in emissions in industrialised countries will encourage the improvement of electricity production technology. The poorer developing countries will have to reduce emissions in the second half of the 21st century, which will have a positive major impact, in addition to the introduction of emission control (such as the installation of desulphurization units), as an improved technology for electricity production, as we have already mentioned. [28]

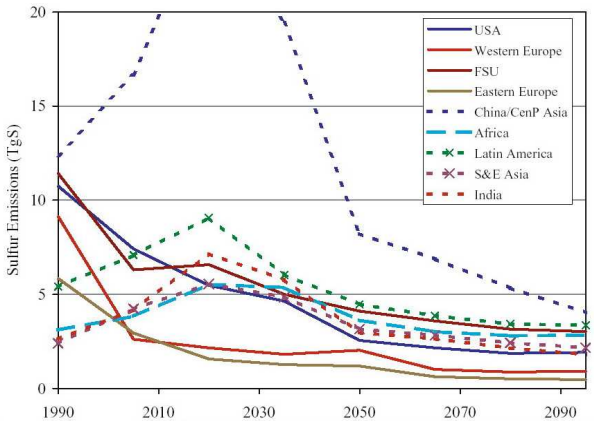

Figure 5 - Global sulphur emissions.[28]

Table 12- Estimated sulphur dioxide emissions in the 21st century.

SO_2 World emissions								
year	**1990**	**2005**	**2020**	**2035**	**2050**	**2065**	**2080**	**2095**
[Tg S]	72	65	78	62	39	33	29	27

2.3.3.2 Emissions in the Czech Republic

After the change of the political system in 1989, legislation such as the Law 309/1991 Sb.o on Clean Air pollutants, introduced emission limits and other conditions for the operation of resources. Detailed regulations seen by the law were based primarily on the legislation from the Federal Republic of Germany, which then represented a set of possible regulations to protect air quality in Europe. As a result of the definition of emission limits, this Act has succeeded in significantly reducing emissions of a wide range of pollutants into the air, such as sulphur dioxide, whose emissions amounted to 2 257 kt in 1980 and dropped to 299 kt in 1999, which was the first year of the full effectiveness of the law.[34]

Figure 6 shows the variations in emissions of SO_2 in the Czech Republic and Slovakia in the period between 1850 and 1994, broken down according to types of fuels. SO_2 emissions from smelting sulphide ore and coal burning were the most important sources before 1870. Since the 80s in the 19th century, the burning of brown coal was implemented, which recorded a significant increase after the Second World War [16].

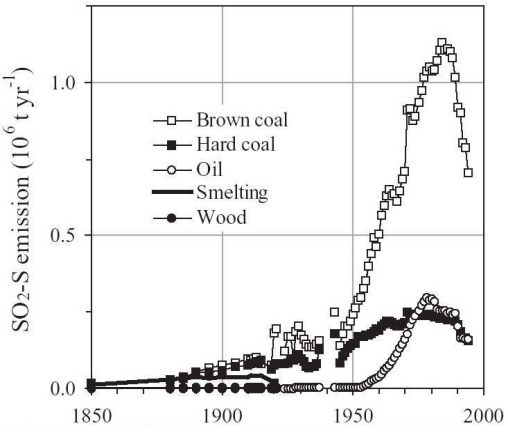

Figure 6 - Sulphur dioxide emission variations from 1850 to 2000.

Figure 7 illustrates the total emissions of SO_2 in the Czech Republic and Slovakia in the period between 1850 to 1994, calculated from data collected on fuel registers and yearbooks.

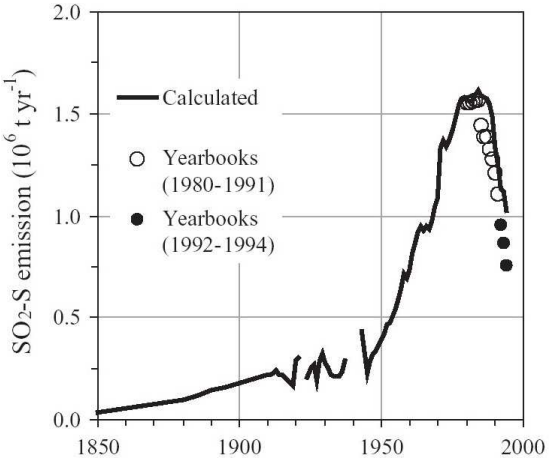

Figure 7 – Sulphur dioxide total emissions in Czech Republic and Slovakia from 1840 to 1994.[16]

The decrease in the emissions of major pollutants since 1989, which is not only a consequence of the entry into force of legislative adjustments to protect the air, but also an attempt to provide more environmentally friendly solutions, namely in the field of the automobile industry, the result of the gradual replacement of natural technologies and of the improvement of the structure of primary energy sources in favour of liquid and gaseous fuels, particularly those presented in Figure 8.

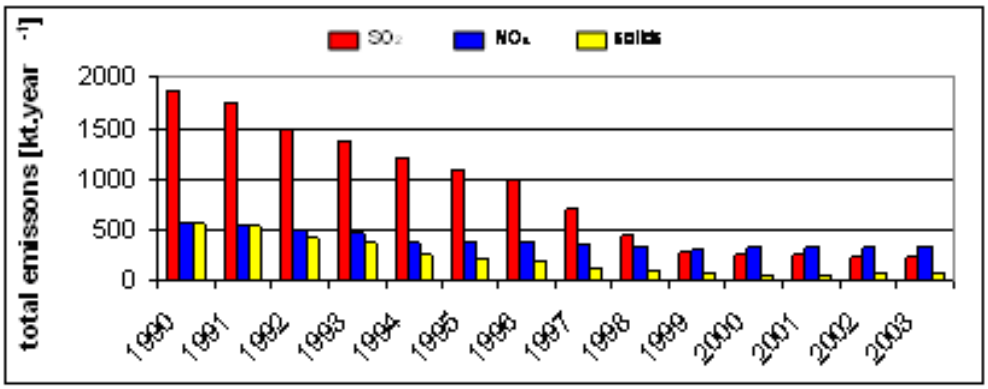

Figure 8 – SO_2 emissions evolution from 1990 to 2003 in the Czech Republic.[38]

Table 13 shows the breakdown of sulphur dioxide emissions according to the source structure in 2001 in the Czech Republic. The table reveals that small sources also have a significant impact on the total SO_2 emissions (due to the amount of small sources of sulphur dioxide).

Table 13 – Total sulphur dioxide emissions according to source type.[38]

Sources of Pollution	Total SO2 emissions in 2001 [kt]	[%]
Large sources	193,4	77,1
Secondary sources	7,5	3
Small sources	43,1	17,2
$\sum$	**250,9**	**100**
Stationary sources	244	97,3
Mobile sources	6,9	2,7
$\sum$	**250,9**	**100**

2.4 Desulphurization processes

The reduction of sulphur emissions can be achieved primarily by removing sulphur from coal, during the combustion process, or later on from the flue gas (after the combustion process).

2.4.1 Coal desulphurization

Sulphur in coal may exist in various forms. The use of physical and chemical processes to separate sulphur from coal is based on different principles.[34]

2.4.1.1 *The physical separation of pyritic sulphur*

Given that materials present different degrees of resistance, it is possible to separate pyritic sulphur from coal, due to coal's different grinding properties and pyrite's resistance in maintaining the original size of a grain.

It is also possible to use the magnetic properties of pyrite and separate it with the assistance of an electromagnet, or, still, explore the differences in the density of coal and ingrown ore, by the use of $BaSO_4$.

Unfortunately, the majority of Czech coal contains a significant amount of ingrown pyrites in the form of small particles, which are difficult to separate.

2.4.1.2 Myer process

The Myer process consists in leaching pyritic sulphur with a water solution of ferric sulphate at 90℃ -130℃. Regeneration of the ferrou s sulphate product is carried out with air oxygen. In this way, pyrites can be effectively separated, but organically linked sulphur remains in the coal.

2.4.1.3 Gravimelt process

The Gravimelt process aims to extract ash from coal fuel with molten NaOH at temperatures which vary between 320℃ to 415℃. The ash contained in coal in an alkaline environment reacts to form silicates, ferrite and sodium aluminates, and is separated from the insoluble coal. Coal is the first to be grinded, and then molten NaOH is added to the rotary kiln. The liquid product is transferred into an aqueous solution; coal is than separated and washed with water. This alkali coal is neutralised by the use of acids. In this way, a complete separation of coal and ashes is almost obtained, remaining approximately 1% of ash in the coal.

The extract containing dissolved ash is neutralized to eliminate the iron and aluminium hydroxides. These are separated and can then be processed in the metallurgical industry into individual metals.

2.4.1.4 Biological sulphur removal

Biological leaching of sulphur from coal has drawn in the mining of copper and vanadium from low-grade ore. This is a desulphurization process carried out by bacteria:

- *Thiobacilus ferrooxidans,*
- *Thiobacilus thiooxidans*.

These bacteria are always present in acid mine water in the vicinity of rocks containing pyrites or marcasite. Acidic water from leaching containing biological H_2SO_4 must be neutralised with CaO or $CaCO_3$.

Bacteriological march is slow and depends on temperature variables. At 16℃ it is virtually stopped. The effectiveness of the process is relatively low and there is no extraction of organic sulphur from coal.

The application of the coal desulphurization process for energy purposes encountered the low efficiency of desulphurization of coal and, hence, the impossibility to comply with limits of emission values. Currently, these processes are unable to compete economically with the desulphurization combustion processes.

2.4.2 Flue gas desulphurization

For the removal of sulphur from power gas (particularly hydrogen sulphide and organic sulphur pollutants), several technological processes were used and developed in the past (depending on the type of power gas, and on the sulphur content of a desired cleaning degree), namely:

• Dry methods (such as cleaning Fe_2O_3 material or activated coal);

• Wet regenerative alternatives (for example: the ammonia process, the ethanolamine process, Sulfinol and Shell-adip, Alkazid, Vacuum-carbonate under low pressure with Na_2CO_3 or K_2CO_3);

• chemisorption with oxidative regeneration (for example, Ferrox, Fischer way, SMO, Perox, Holmes-Stredford, Giammarco-Vetrocoke, Sulfin);

• Physical sorption (Sorption with cold water, Rectisol, Purisol).

2.4.2.1 *Rectisol*

Rectisol works on the principle of absorption of undesirable components in the gas (H_2S, CO_2, COS …) by methanol at low temperatures. With the decreasing of temperature, methanol's absorption capacity rises very quickly.

Raw gas is purified in three stages:

• In the first stage of the scrubber, the hydrocarbons are washed out with water which contains a small amount of methanol (at around 0℃) .

• In the second stage, the sulfan is selectively washed out with a precisely defined amount of methanol (temperature around -50℃).

• In the third stage of the scrubber, the carbon dioxide and methanol are washed out (at a temperature of around -70℃).

The advantage of this method is the removal of all impurities, which would otherwise have to be absorbed in many ways. Methanol is almost unable to dissolve flammable gas components (H_2, CO, CH_4), which would diminish the calorific power of the fuel. In Sokolov, coal a.s. Vřesové is built in an integrated gas-steam cycle, which uses the Rectisol process. For the purpose of generating electricity, the power gas, which is obtained in pressure generators (steam-oxygen Gasification of brown coal), is produced first. The combustion turbines are regulated so that they can burn both gases: the power gas obtained from the brown coal and from natural gas. Power gas, after being desulphurized, is included in the combustion chambers of gas turbines. Regeneration of methanol is further processed into high quality sulphuric acid.

$$2H_2S + 3O_2 \Leftrightarrow 2SO_2 + 2H_2O \quad (13)$$

$$2SO_2 + O_2 \Leftrightarrow 2SO_3 \quad (14)$$

$$SO_3 + H_2O \Leftrightarrow H_2SO_4 \quad (15)$$

This method of desulphurization which is applied to the final product of coal gasification is a cost-effective solution, because it cleans much smaller volumes of gas than the percentage which results from the burning of coal, because the sulphur content in the clean gas is around 1 ppm. The product of desulphurization is a very pure sulphuric acid (there is no problem the retailing of the by product).[30,37]

2.4.2.2 *Flue gas desulphurization*

Unlike desulphurized coal, desulphurization of flue gases is established through an industrial process. Desulphurization technologies for flue gases can be characterised by significant volumes of purified gases, low concentrations of pollutants in the exhaust gas, which are SO_2, SO_3, Cl^- and F^-, and enormous mass flows of these substances.

Production of flue gas depends on the type of combusted fuel and on the surplus of combustion air. The usual values of production for the production of 200 MW combustion of electricity per-standard conditions are:

• **Brown coal** roughly 1.0 to 1.2 million $m^3.h^{-1}$

• **Black coal** approximately 0.7 million $m^3.h^{-1}$

• **Liquid fuels** in the order of 0.5 to 0.6 million $m^3.h^-$

High volumes of exhaust gas to purify leads to cost disadvantages, because these require specifically dimensioned devices. Higher sulphur content in coal leads to higher emissions of sulphur oxides, which must be separated from the flue gas. Large quantities of desulphurization products are difficult to use.[34]

Flue gas desulphurization can be classified as:

• Non-renewable because the reagent in the scrubber is consumed in order to directly generate a by-product containing the sulphur, such as gypsum.

• Renewable - the spent reagent is regenerated in a separate step to renew the reagent material for further use and to produce a separate by-product, such as elemental sulphur.

Another form of classifying the desulphurization process is its distribution in the categories of dry and wet:

• Wet - SO_2 is absorbed, essentially using alkaline substances.

• Dry - sorption and catalytic processes, take place on the sorbent surface or catalytic converters at temperatures above 100℃.

• Semi dry - the active substance - water lime - is injected, in the form of water suspension, into the current hot gases, the liquid then evaporates and the reaction product is absorbed in a solid state.

The final criterion is the physical or chemical nature of the process under which the desulphurization methods can be divided: absorption, adsorption and catalytic.[34]

2.4.2.3 *Dry methods*

In these methods, there is a heterogeneous solid-gas reaction. The process can be applied to flue gas desulphurization for the classic boilers or for fluidized bed boilers.[34]

2.4.2.3.1 Flue gas desulphurization using limestone in pulverized coal boilers

Flue gas desulphurization consists of dosing fine grinded limestone and air into the combustion chamber in the boiler. The process takes place as described below:

$$CaCO_3 \xrightarrow{>850\,^{\circ}C} CaO + CO_2 \qquad (16)$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (17)$$

Limestone's calcinations take place at temperatures above 850℃; the reaction between CaO and SO_2 takes place at greater speed between 600℃– 1100℃ . Above this temperature, there is a deactivation generated as a result of changes in the porous structure. Limestone must be sufficiently grinded, at least 90% of particulate matter should be <60 μm. The product of the reaction is $CaSO_4$ in addition to a significant amount of unreacted CaO of limestone and fly ash from coal combustion. The SO_2 comes into contact with the particles of calcium oxide, and diffuses through the porous, reacting, and the $CaSO_4$ acts as a wall around the surface of the sorbent against the diffusion of more molecules of sulphur dioxide. The result is that the conversion of the generated CaO is low and varies from 11 to 15% (stoichiometry CaO:SO_2). The contact time for the particles to react in the boiler is low, usually a few seconds, depending on the boiler structure and level of use of installed capacity. The advantage of this process is the low investment in technologies (machinery).[34]

Given that the application of limestone in the pulverized coal boiler cannot achieve high conversion due to the limited residence time, in fluidized bed boilers, this period of time, on average, may reach the time of one thousand seconds. Sulphation happens at an optimal temperature which varies between 800℃ to 8 50℃. This technology also applies to longer SO_2 diffusion through the $CaSO_4$ layer in the porous structure. This layer leads to abrasion of the grains and, in this way, accelerates the diffusion of SO_2 into the unreacted CaO.

A fluidized burning fuel is a technology that will replace today's classic generation of powdered coal boilers. It can also burn coal with low calorific value, which is quite difficult in powder burning boilers. Fluidized-bed combustion, when compared to the classic powdered coal, has higher energy efficiency rates.

2.4.2.3.2 Active soda

This method has a non-renewable character. Decomposition of sodium bicarbonate ($NaHCO_3$) takes place at 90℃, and generates a highly react ive Na_2CO_3, which reacts easily with the SO_2 in the flue gas to produce sodium sulphite (Na_2SO_3), with a smaller proportion of sulphite oxidized to sulphate.

In contrast, for dry limestone additive technology, this process has the same "solid-gas" reaction mechanism but with a higher conversion of Na^+. This is due to the fact that Na_2CO_3 results from the calcination of $NaHCO_3$ showing higher reactivity.

2.4.3 Semi dry lime method

The semi dry lime method consists in injecting lime water into the reactor, which is an atomization chamber. The process consists in the adiabatic evaporation of water from the suspension and the cooling of exhaust gases at an optimum temperature reaction:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \quad (18)$$

In addition to calcium, sulphite is formed by the oxidation of a small quantity of calcium sulphate:

$$2CaSO_3 + O_2 \rightarrow 2CaSO_4 \quad (19)$$

The product is separated by electrostatic precipitators (ESP), or bag house filters, sometimes requiring the reheating of the flue gas (to avoid condensation inside the stack). In this desulphurization process, it is important that, combustion temperature closely approximates the dew point of water. In addition to the suspension of the lime, it is possible to achieve the required temperature by adding water.
A modification of this process is caused by the absorption of sulphur dioxide lime in the fluidized-bed. Flue gases from the boiler (after the dust collection) enter the fluidized bed reactor, in which the fluid layer consists of calcium hydroxide. The optimum temperature in the reactor is maintained so as to achieve the adiabatic evaporation of water. The product is partially recirculated in order to guarantee a better use of lime.[34]

2.4.4 Wet methods

Wet methods of desulphurization can be divided into several types depending on the kind of absorption suspension.[33]

2.4.4.1 *Lime-sludge suspension type*

SO_2 is removed into water suspensions of CaO creating an insoluble sludge, which contains gypsum - dehydrate calcium sulphate ($CaSO_4$. $2H_2O$), hemihydrates calcium sulphite ($CaSO_3$. $½H_2O$), calcium sulphite ($CaSO_3$) and no reacted part of lime. The

disadvantage of this method is that the product is not chemically stable and constitutes a challenging for storage.

2.4.4.2 Lime-gypsum suspension type

SO_2 removal with water suspensions of CaO is done in two stages. First, $CaSO_3.½H_2O$ is formed; then, the pH of the suspension reaction is adjusted through the use of sulphuric acid and in the oxidative reactor, the first compound is oxidized by air, hence forming gypsum ($CaSO_4.2H_2O$).

2.4.4.3 Limestone - gypsum suspension type

The limestone - gypsum suspension type consists in the wet scrubbing of the combustion flue gases with finely minced natural limestone. SO_2 reacts with limestone suspensions forming sulphite which, in an acidic medium, is oxidized by oxygen in order to create sulphate. The desulphurization technology more frequently used in power plants in the Czech Republic is the wet limestone method, which is certified and economically sustainable.

Given that this work focuses on the wet flue gas desulphurization using limestone suspensions, this topic shall be discussed in greater detail in the following sections.

Comparison of desulphurization efficiency of different methods is presented on Table 14.

Table 14 - Comparison of desulphurization efficiency of different methods.

Desulphurization methods	The effectiveness of flue gas desulphurization [%]
Dry fluidized bed combustion technology	80-90
Semi dry limestone method	60-90
Wet limestone method	≤ 96

2.4.5 Regenerable processes

In regenerable processes, the sorbent is reused after thermal or chemical treatment to produce concentrated SO_2, which is usually converted into elemental sulphur. These are complex processes requiring high investments (wellman-Lord process, magnesium oxide).

2.4.5.1 Sodium sulphite process

The raw material used for this process is NaOH or Na_2CO_3. With the absorption of SO_2 sodium sulphite is formed, which also reacts with the SO_2 to form sodium bisulphite:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \quad (20)$$

This reaction releases heat. By the reaction polysulphides are formed, a heavily polluted sodium sulphate decahydrate. Given that sodium sulphate does not react with SO_2, it is undesirable and inhibits the addition of EDTA. Excess of sodium sulphate has to be taken from the absorption solution. The absorber and regenerator must be made of high-alloy materials, mostly steel Cr-Ni-Mo.

2.4.5.2 Magnezit process

In this process, input raw material is MgO prepared by calcination of natural mineral magnesium carbonate ($MgCO_3$), or MgO from sea water. The reaction mechanism is similar to that of the sodium sulfite process which forms Magnesium sulphite:

$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2 \quad (21)$$

$$Mg(HSO_3)_2 + MgO + 5H_2O \rightarrow 2MgSO_3.3H_2O \quad (22)$$

Ancillary reaction (oxidation) happens in order to form magnesium sulphate. The trihydrated product is then dried at about 170ºC and $MgSO_3$ is obtained, then being calcined at higher temperatures. MgO returns to the cycle and SO_2, which is obtained from the regeneration in concentrations from 16% to 18%, is treated with sulphuric acid contact. For the purpose of processing the elemental sulphur, concentrations are considered inappropriate.

2.4.5.3 *Water- carbonates process*

In this process, Na_2CO_3 solution is sprayed into the combustion chamber; the final product of this dry desulphurization process is a mixture of sulphite and partly sodium sulphate. This product then melts the coke to produce sodium sulphide and CO_2. The melted substance is dissolved in water, filtered and introduced into the solution of CO_2 to form H_2S and sodium bicarbonate. H_2S is processed to elementary S. $NaHCO_3$, is heated to form Na_2CO_3 which returns to the process. The absorption takes place at a temperature of 90ºC; it is not necessary to warm up the exhaust gases. Losses of the reagent are significant and are approximately 0,1 mol Na_2CO_3 for 1,0 removed mole of SO_2.

2.4.5.4 *Citric acid process*

Sulphur dioxide is removed using a sodium citrate solution for the creation of Na_2SO_3 and Na_2SO_4 formed by an oxidation reaction. Absorption of SO_2 takes place at low pH (about 3.1), in which the oxidation of SO_3^{2-} to SO_4^{2-} takes place at a large scale. The recovery of the saturated absorbing solution can be done in two ways:

• The introduction of H_2S to exclude elemental sulphur (the by-product formed is $Na_2SO_4.10\ H_2O$, which must be removed from the system)

• Desorption of SO_2 requires the use of a heat exchanger to warm up the medium temperature.

2.4.5.5 *Desulphurization using active carbon materials*

Active carbon materials are suitable for the removal of sulphur dioxide from flue gases, because of their high-quality sorbent structure (big surface area).

They can be used in flow-through and in recovery processes. In regenerable processes high quality black coal (active coke) is used; however, in once-through processes, significantly cheaper brown coal can be used.

Desulphurization takes place on the surface of active carbon materials by catalytic reactions; in the porous surface, the SO_2 is adsorbed and reacts with O_2 and steam in the flue gas creating H_2SO_4. The reactions take place in temperatures ranging from 80^oC to 140 ^oC, but the ideal temperature is from 100^oC to 120^oC. Regeneration is carried out at

high temperatures, approximately 450^{o}C, where the degradation of sulphuric acid carbon takes place.

Regeneration generates concentrated SO_2, which may contain halogens and heavy metals (Hg, As, Sb, and others), being capable of handling both the elemental sulphur, as well as sulphuric acid.

2.4.5.6 *The dual alkali process*

Input raw material in this process is NaOH or Na_2CO_3. SO_2, which is removed from the flue gas forming Na_2SO_3, which is then transformed into $NaHSO_3$. The raw material is then regenerated by the addition of $Ca(OH)_2$, which creates a mixture of calcium sulphate, calcium sulphite and NaOH.
The advantage of this process is that there is no formation of an undesirable product such as Na_2SO_4 in the process. The product may be use as construction material or plaster as a stabilizing agent, as in wet limestone technology.

2.4.5.7 *The Walther & Cie*

The Walther & Cie is a process that uses ammonia. The sulphur dioxide reacts and ammonium sulphite is formed. It is oxidized by air into ammonium sulphate. The removal of SO_2 consists of two series: the first consists in counter flow removal devices, while the second stage includes a scrubber reactor, which has an oxidizing air pump. The solution is sprayed over the gas stream and crystalline ammonium sulphate is obtained. The final product can be used as fertilizer for agriculture. The disadvantage is the need for deep cooling of exhaust gases (up to 30^{o}C) and the formation of white matter of ammonium sulphate, which colours the flue gas on the outlet of the stack.

2.4.5.8 *Biological flue gas desulphurization (BIO-FGD)*

Biological flue gas desulphurization consists of a combination of absorption of SO_2 by sodium hydroxide in the following two biological processes: i) first, in an anaerobic reactor where $NaHSO_3$ is reduced to NaHS, which in subsequent aerobic reactor provides elemental sulphur. The reaction takes place at pH 7 to 8, as the electron donor is an organic compound (ethanol); ii) H_2 is required to reduce SO_2 and to obtain the cleavage of

methanol or natural gas. During the process, the separation of sulphur excluded initially takes place concentrating on a sedimentation tank and subsequently dewatering into a vacuum filter.

2.5 Wet limestone method

The principle consists in the absorption of sulphur dioxide in a water suspension of limestone, which takes place preferably at a temperature of approximately 60℃:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4.2H_2O + CO_2 \quad (23)$$

In the continuation of this process, as described in equations 24-29, SO_2 is absorbed in the limestone suspension, the dissolution takes place and the group Ca reacts with SO_2 generating the sulphites which are then oxidized by the air. This process originates the formation of sulphates. This process shall be discussed in greater detail in further chapters.

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad (24)$$

$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + H_2O + CO_2 \quad (25)$$

$$CaCO_3 + H_2O + 2SO_2 \rightarrow Ca(HSO_3)_2 + CO_2 \quad (26)$$

$$Ca(HSO_3)_2 + CaCO_3 \rightarrow 2CaSO_3 + H_2O + CO_2 \quad (27)$$

$$CaSO_3 + 2H_2O + \frac{1}{2}O_2 \rightarrow CaSO_4 \cdot 2H_2O \quad (28)$$

$$Ca(HSO_3)_2 + H_2O + \frac{1}{2}O_2 \rightarrow CaSO_4 \cdot 2H_2O + SO_2 \quad (29)$$

The critical step on this mechanism is the resistance against SO_2 diffusion in the liquid phase, and in this way the dissolution speed of limestone. This process can be accelerated by:

• reducing the particle size and increasing the limestone surface (finely grinded with a typical grain size of 90 - 100% <40 μm);

• increasing the stoichiometric proportion $CaCO_3$: SO_2;

• increasing the proportion liquid to gas ratio L/G (the ratio between suspension volume and flue gas volume under standard conditions);

• the use of additives (organic acids, Mg^{2+});

• maintaining an acid pH (the disadvantage is that with pH <5 the Al^{3+} is not captured on the ash in the absorber and, thereby, reacts with fluorine ion and AlF_6^{3-} ion is created, which causes scaling in the absorber environment and precipitates on the drops).

This method shows high desulphurization efficiency (up to 96%). In addition, it removes 90% of hydrochloric acid from flue gases, from 70% to 95% hydrofluoric acid, 70% to 90% of ash that is not captured in the filters, approximately 10% of NO_x and up to 95% of trace compounds, heavy metals and toxic compounds. The disadvantage is the waste water containing chlorine (order of ten $g.dm^{-3}$), fluorine (order of hundreds $g.dm^{-3}$) and sulphate (order of units $g.dm^{-3}$) ions.

2.5.1 Technology of wet desulphurization using limestone

Technological devices (smoke flue stack, heat exchangers, namely, flue gas, absorbers, fans and pumps) may vary in the design and placement of the desulphurization system(see figures 9 and 10).[34]

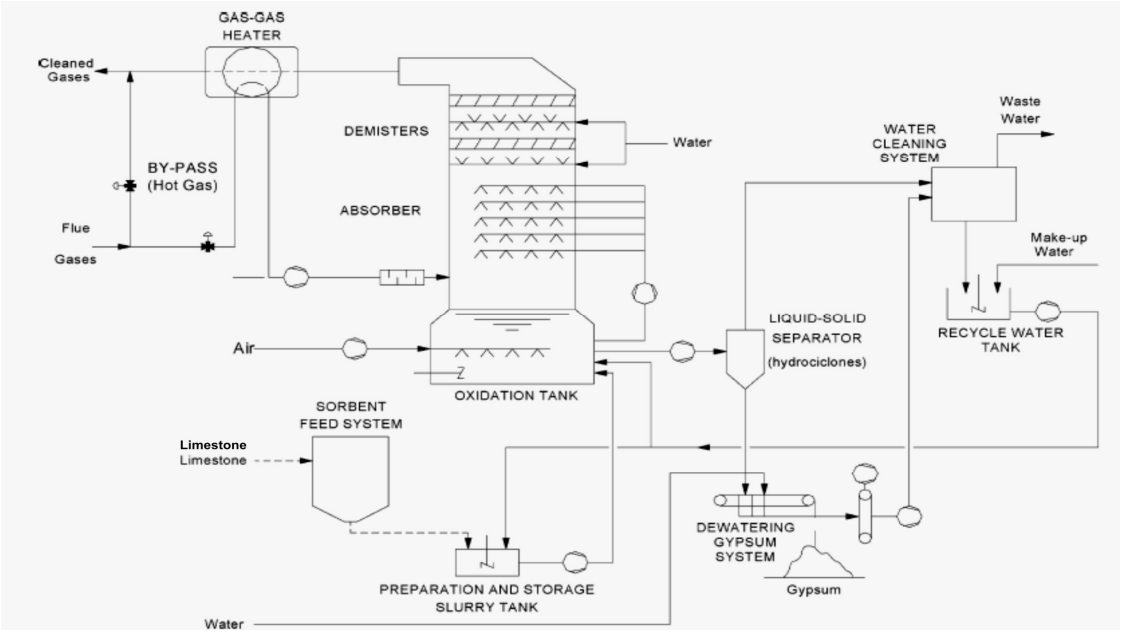

Figure 9 – Desulphurization unit with shower absorber diagram.[42]

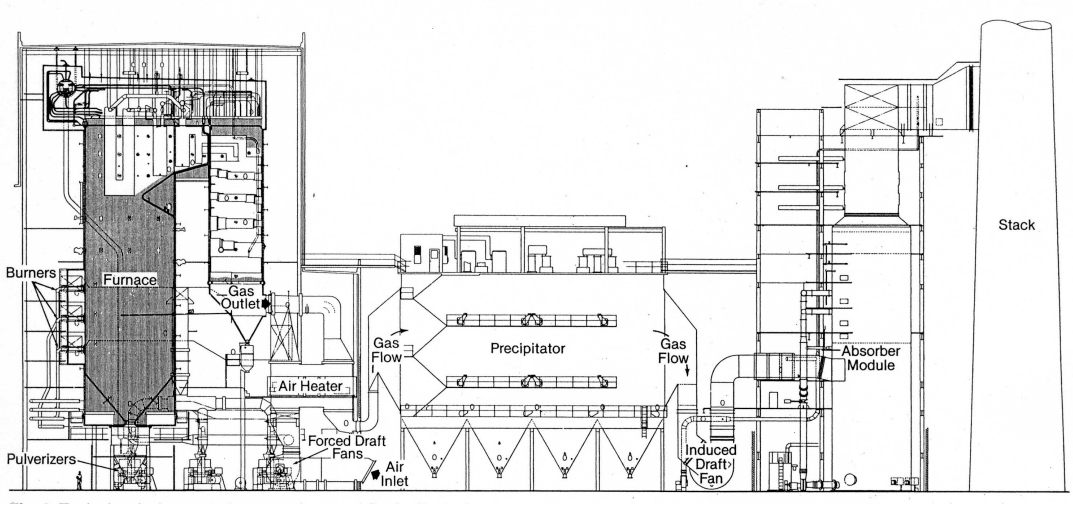

Figure 10 – Typical coal powered thermal plant design.

2.5.2 Smoke stack

Structural steel for the smoke stack construction is used. On the hot section of the stack, (before sulphur removal), is not protected against corrosion because the temperature of the flue gases is higher than the dew point of sulphuric acid. On the cold section (after sulphur removal) the stack must be protected against corrosion, with wall materials which are acid resistant. The external hot part has to be provided with thermal isolation materials. [34]

2.5.3 Heating and combustion

The flue gases leave the electrostatic precipitator (ESP) with temperatures ranging from 120℃ to 170℃ which is why they must be cooled for the application of wet desulphurization processes. Part of the heat can be economically used for heating desulphurization flue gas; the remaining heat is used for adiabatic water evaporation from the absorption suspension. Combustion heat exchangers are expensive, but are a good investment for high capacity power plants, given that the flue gases are heated by the use of steam, or heated air, or by the optimization of the heat from the combustion of low sulphur fuels. In recent years, the so-called wet chimneys were used, which scatter combustion exhaust gases without heating.

Heat exchangers (heat transfer) can be divided into two categories: regenerative and recuperative.[34]

2.5.4 Wet scrubber

The contaminants are removed from the flue gas by passing the stream through a packed structure which provides a large wet surface area that induces contact between the gas and the scrubbing suspension. The contaminant is absorbed into or reacts to the scrubbing suspension. The design of the tower is done in order to encourage the dispersion of the liquid flow without tracking, to provide maximum contact area for the mass transfer interaction and to offer minimal back pressure to the gas flow. Minimal pressure drop means less energy is spent in the transportation of the gaseous stream.

The absorber structure is made up of three basic parts:

• Absorption sink (which is focused on the suspension to absorb the SO_2, fresh suspension is brought to the sink to replace the product formed - $CaSO_4.2H_2O$, and oxidation air is delivered for the oxidation of sulphite into sulphate. Content is mixed by a stirrer; pumps are used for the oxidizing of the air and to take the absorption suspension to the shower nozzles).

• The absorption zone (stream of gas comes into contact with scrubbing suspension).

• Drop separators (the purpose is to create a spray based on the separation liquid - a well-designed trap achieves the L/G values around 35 to 50 $mg.m_n^{-3}$). The traps most commonly used are crash separators. They are a number of boards diagonally deposited in the direction of the gas (which change the direction in which the gas flows and the drop separators are washed by water, to avoid clogging).

According to the flow, three types of absorbers can be distinguished: co-current, current and combined. Wet scrubbers, used in industries which emit sulphur dioxide, can be divided into four basic types: [34,41]

• shower (tower - the exhaust gases are going in counter current of suspensions);

• filling (the stream gas and the suspension have the same flow direction);

• bubbling (combustion products are introduced below the level of absorption suspension to create foam, in which a considerable mass transfer occurs)

• co-current and counter-current (combustion gas first enters the absorber from the top, following the direction of the liquid where it is sprayed on several levels with the suspension, over the direction of the flow, then turns counter current for a further "shower" with scrubbing suspension via drops separators).

Most of the absorbers are constructed from structural steel and the surface is corrosion-resistant made from different materials (rubber, glass-fibre, reinforced resin or special alloys, and high-alloy steel). High jets that spray the suspension are made of nickel steel and joints are made from abrasion-resistant materials such as SiC or MoS_2.[34]

Figure 11 provides an example design of a spray absorber. In the scrubber, under the shower levels, there is a perforated board where the exhaust gases flow, which usually has an approximate speed of 3 $m.s^{-1}$, the pressure losses range from 0.2 kPa to 0.7 kPa, the ratio of L/G is around 20 $dm^3.m^{-3}$. Working pressure suspension on the spray nozzles is usually situated between 35 kPa to 140 kPa. Average diameter size is about 2000 μm to 2500 μm and length of the residence time is of approximately 1 to 3 s.[1]

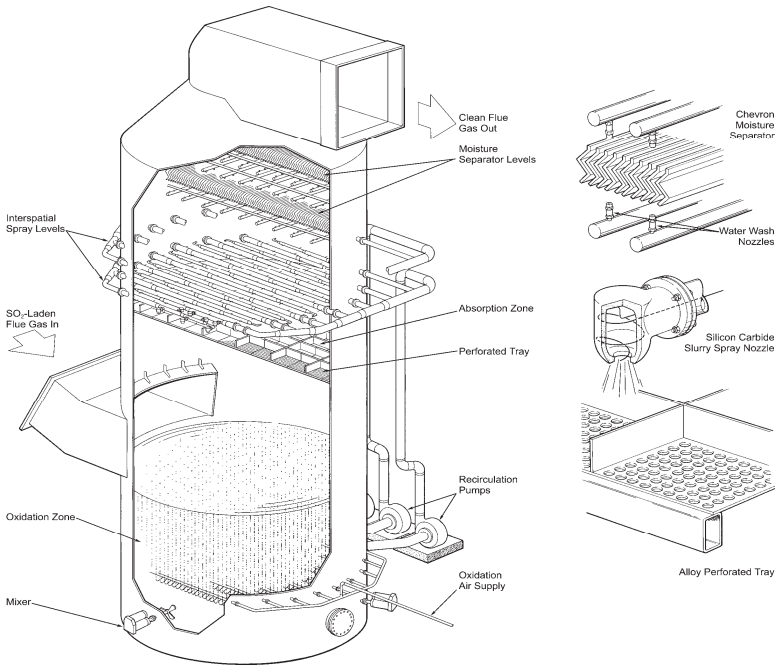

Figure 11 – Wet scrubber.[1]

2.5.5 Centrifugal pumps

Centrifugal pumps are specially developed for the transportation of any kind of suspensions. Pumps are to have at least 12 to 15 thousand operating hours. Circulating pumps are the units which have the largest energy consumption in the desulphurization unit (because of the necessary L/G ratio and to minimise the pressure drop). A total absorber block on the performance of 200 MW consumes approximately 2-3,6 MW 2-3 MW in the use of circulator pumps.[34]

2.5.6 Fans

The fans have the purpose of assisting the pressure drop of the desulphurisation equipment. The greater the pressure loss of the desulphurization unit, the greater the consumption of electricity. The fan can be placed on the hot (radial, may not be protected against corrosion) or cold flue gases. In more recent concepts axial fans are preferred and installed as decanter drops.

After going through the desulphurization process flue gas goes to the chimney or refrigeration tower, whatever it is more advantageous for the operator.

2.5.7 Waste water from the wet limestone methods

When compared with the total output of waste water from power plant, the volume of waste water from a desulphurization unit is not significant. The production depends mainly on the requirements for purity of gypsum, for 200 MWe it is within 3 to 21 m^3/h. Waste waters from desulphurization process contain chlorine ions, fluorine and sulphate, and heavy metals from limestone and coal, whose content is limited to the range of 10,4-10,6% wt.[34]

2.6 Parameters affecting the desulphurization process

Wet flue gas desulphurization (limestone method) is a very complex process, which is affected by several factors. Technological development aims to optimize the process for

achieving the highest possible desulphurization efficiency under acceptable operating costs.

The parameters affecting the desulphurization process include, in particular, the construction of an absorber (of the scrubbing suspension type), pH of absorbing suspension, the inlet concentrations of sulphur dioxide, the temperature in the reactor, L/G ratio on the absorber, diameter of scrubber, and, also, for example, the concentration of chloride ions in suspension.

To illustrate what was previously discussed, Y. Zheng [41] suggests the following the changes for a pilot bubble reactor: when the absorption suspension pH increases from 3.5 to 5.5, the desulphurization efficiency also increases from 66.1% to 71.5% (as a result of shifting the balance of SO_2 dissociation in the water for the benefit of HSO_3^-). The addition of chloride ions (in the form of $CaCl_2.2H_2O$) to the suspension (with a concentration of 25g $Cl^-.dm^{-3}$) increased the efficiency up to 99% (due to a considerable increase in the creation of foam and hence an increase the gas-liquid interphase area). Increasing input concentrations from 502 ppm to 991ppm SO_2 leads to a decrease in efficiency from 80.1% to 69.4%. The proportion of unreacted limestone in the desulphurization final product (gypsum) increases with the rise of pH rising on the input SO_2 concentration, and also with the increase of Cl^- concentration on the suspension.

Another factor affecting efficiency is the number of shower levels (in this case the scrubber shower tower). Increasing L/G (L - the amount of suspension expressed in litres, G - the quantity of exhaust gas, expressed in m^3) increases the desulphurization efficiency as demonstrated by Nygaard, [20] after measurements in the coal fired power plant ENERGI E2 A / S in Denmark (with low sulphur content), the absorber has a diameter of 17.5 m and is 51 m of height (see Figure 12).

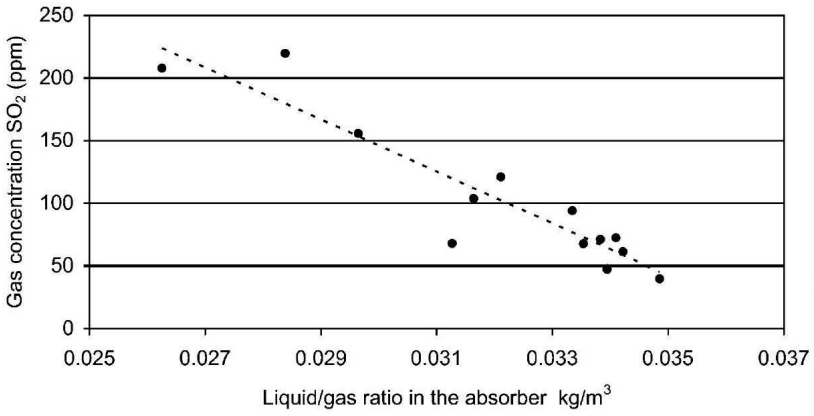

Figure 12 – The decrease on the sulphur dioxide concentration by increasing L/G ratio.[20]

The degree of desulphurization increase is related to the increasing number of levels located above them (see Figure 13).

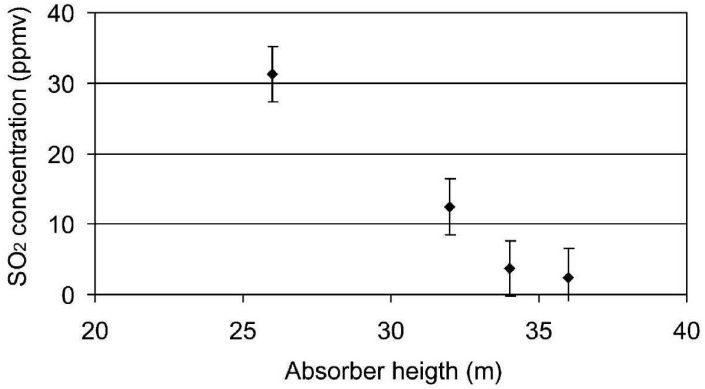

Figure 13 – Decrease in SO_2 concentration according to absorber's height.[20]

The horizontal concentration profile of SO_2 in the scrubber is not the same given that the concentration of SO_2 decreases as the distance from the walls becomes greater.

The influence of the presence of HCl in the flue gas is shown [13] according to the measurements in the co-current reactor with a film suspension falling along the inside wall of the column. The presence of HCl in the flue gas reduces desulphurization efficiency and increases the unreacted limestone in gypsum. One of the ways to prevent such an effect is to add buffers such as adipic acid to the system (see Figure 14).

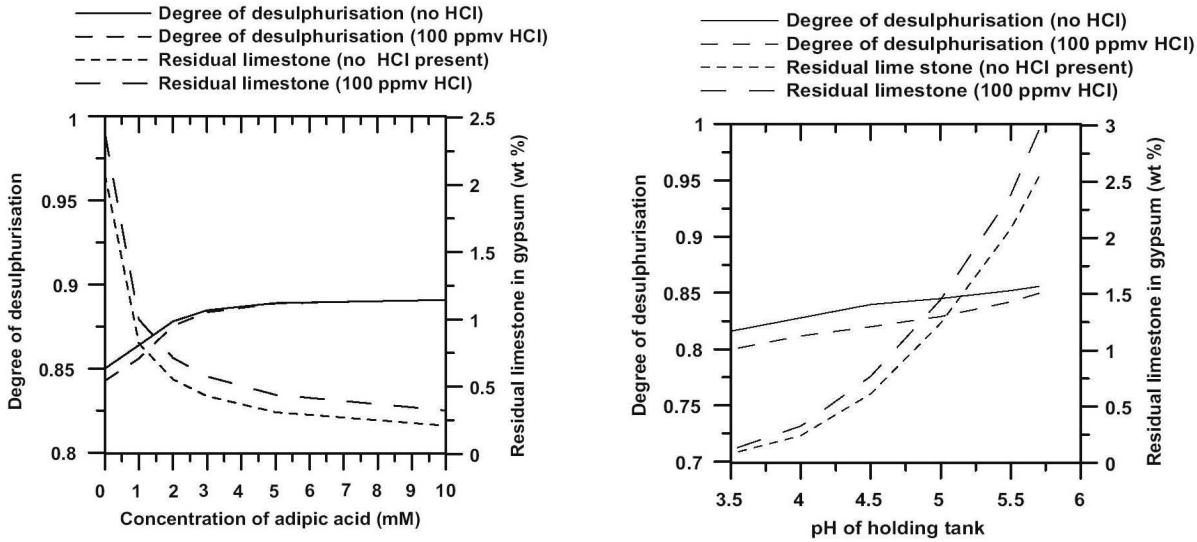

Figure 14 - Degree of desulphurization and unreacted limestone in gypsum and on the absorber's pH as a result of the addition of adipic acid.[13]

Regarding the SO_2 absorption, a certain percentage of sulphites which are not oxidised into sulphates (usually 15% of the captured sulphur dioxide) always remains. In Japan and Europe, the limestone based wet FGD is operated mainly by forced oxidation, due to the fact that the oxygen in the air reacts with sulphite to compose sulphate (gypsum $CaSO_4.2H_2O$), which is used in wallboard manufacturing and in the cement industry. The absorption of sulphur dioxide through the use of limestone suspensions, without resorting to additives, always works at saturation state, which blocks the solubility of calcium sulphate dehydrate. The oversaturation degree μ of the suspension can be expressed as:

$$\mu = \frac{a_{Ca^{2+}} . a_{SO_4^{2-}}}{K_{CaSO_4}} \qquad (30)$$

Where $a_{Ca^{2+}}$ and $a_{SO_4^{2-}}$ indicate the activities of the ions, and K_{CaSO_4} the solubility of the product. Oversaturation degree should not be higher than 1,3 -1,4. If it is higher, this leads to the formation of a large number of crystals, which settle on the absorber walls, and on the drop separators. Therefore, achieving the optimum value of μ is important in terms of trouble-free operation. Should the value of μ oversaturation rate be lower, then there are smaller and less crystals which drain the water. The addition of additives (which are typically organic acids that form soluble calcium salts - essentially dicarboxylic acids) to, equipment used, for example, for the production of $CaSO_4.2H_2O$, is a hypothesis which allows the equipment to work with an unsaturated solution such as $CaSO_4.2H_2O$. The resulting crystals are used in the processing of plaster building materials, but with dewatering requirements. The advantage of using additives is the significant reduction in electricity consumption for propulsion (by circulation pump) of suspension due to the possibility of reducing the ratio liquid gas L/G. The non-additived process works in saturation state from 15-25 $dm^3.m_N^3$, which contrasts with the results achieved by the use of additives, namely 2-3 $dm^3.m_N^{-3}$.[35]

2.6.1 Limestone

For the desulphurization process, limestone containing at least 90% of $CaCO_3$ is used. The particles have to be milled to a size below 40 μm. Power and heat are generated either from limestone gravel from sizes 2 to 6 cm (often wastes resulting from the

production of lime), which can be grinded *insitu*, or else fine limestone can be bought for fort his purpose.

2.6.1.1 *Physicochemical properties of limestone*

Limestone is a sedimentary rock with a diverse chemical composition and different physical properties. According to the way in which it is created, it is possible to distribute limestone according to the following categories:

- chemical sediments (resulting from the equilibrium in the system CO_2-H_2O-CaO);
- organogenic sediments (remnants form calcic shelling of prehistoric organisms);
- metamorphosed (converted).

Non-metamorphosed strata limestone is usually complete (such as limestone Moravia and Slovak Karst). Occasionally, there is sandy limestone, such as in Koněprusy. Crystalline limestone is located in converted strata (e.g. gneiss and crystalline slates).

Pure $CaCO_3$ is rarely found in nature. However, it is widely produced, throughout the world, into different admixtures. The main mineralogical component of limestone rocks is calcite. This mineral is the most common mineral in addition to silica. It crystallizes in the hexadic system, mostly in the form of rhombohedra and often creates double strips. It has a perfect cleavage angle with clear double refraction. It is a fragile mineral with a density of 2,7-2,8 $g.cm^{-3}$ and a hardness of 3rd. It can be found in sedimentary rocks, in crystalline slates and weather-worn eruptive rocks, as well as in all geological formations from the younger Precambrian. In addition, the $CaCO_3$ in the form of aragonite, crystallises in a diamond shape system. Cleavage of this material is imperfect; the specific weight is 2,9-3 $g.cm^{-3}$ and hardness is 3,5-4. Limestone was built mostly as a secondary mineral in eruptive rocks or sediment from mining and eruptive hot water. The most common form of limestone is calcite and aragonite. Limestone with macroscopic grains is marble. Limestone occurs more frequently in the form of microcrystalline. Only the purest limestone is white, because it containing different components which lead to changes in colour.

Chalk sediments are found in the Cretaceous geological period and, therefore, are considered young rocks, unlike the Cretaceous limestone rocks that are characterised by their fragile nature. The contents of $CaCO_3$ in chalk is high (89-99%) and there are only a residual concentrations of SiO_2, Al_2O_3 and $MgCO_3$ in the limestone. Limestone which

contains silica, aluminium and iron admixtures is hard, giving the necessary characteristics to be transformed into clay. Geologic sediments resulting from the current sedimentation process of $CaCO_3$ and loam substances make hard limestone. This kind of limestone often contains bituminous shares from organic origin and their colour goes from yellow to gray.

Limestone often forms a solid row, in conjunction with any other rock (clay, dolomite, sandstone, siderite, ...) and their mutual relationship ($CaCO_3$ content and other rocks) may be filed (such as limestone, dolomitic limestone, calcite dolomite, dolomite).[31]

According to the chemical composition of limestone, it can be divided into 7 grades according to CSN 721217 (see table 15).

Table 15 – Limestone distribution into classes according to CSN 721217.

Contents[wt.%]	**Class**						
	I.	**II.**	**III.**	**IV**	**V.**	**VI.**	**VII.**
$CaCO_3$+$MgCO_3$ at least	98.5	97.5	96.0	95.0	93	85	80
$MgCO_3$ maximum	0.0	0.8	2	4	6	10	15
SiO_2 maximum	0.3	0.8	1.5	3	4.5	6	8
Al_2O_3 + Fe_2O_3 maximum	0.2	0.4	0.8	2	3.5	5	6
Fe_2O_3 maximum	0.03	0.1	0.3	1	2	2.5	2.5
MnO maximum	0.01	0.03	0.03	0.03	-	-	-
SO_3 maximum	0.06	0.1	0.2	0.2	0.3	0.5	0.5

According to the limestone's structure it can be divided into the following:

• sandy- crystalline, marble;

• compact (grains linked by various substances which create a fine sandy rock with a crystalline structure);

• oolitic (other grain-related)

• limestone ash rock (has a distinctive porous structure, resulting from the dissolution of Ca $(HCO_3)_2$)

• marble limestone rocks (soft limestone rocks)

• Cretaceous (very soft limestone rocks)

Limestone is used in the manufacturing of building materials (lime, cement, building and decorative stone, etc.) in metallurgy, in the chemical industry, in food, in the desulphurization of thermal power, agriculture and other fields (glass, ceramics, etc.).

2.6.2 Limestone bearings in the Czech Republic

The Czech Republic is relatively rich in limestone materials, but their use is largely limited to quality, geological conditions and "conflicts" with environmental protection requirements. The Czech Republic Geofond has information and documentation regarding the geological state service: in 1997, 103 limestone deposits were registered, of which only 26 have been extracted. These deposits are distributed unevenly in different geological units as the following list describes in a summarized manner:[7]

Devon Barrandienu, Central Bohemia

Devon Barrandienu is a classical area for the occurrence and use of limestone. Bearings are mainly from the pre-Devonian, and partly from the Silurian age. There are many types of limestone, which characteristically have a high content of calcium carbonate from the koněpruského Reef. It is quite frequent to find limestone in the state of transition into dolomitic limestone and clay. The area is an important source of limestone with a high percent of calcium oxide which cater for its demand in the production of high quality lime. Cement is produced with the sub-sieved fractions and other limestone. On the whole, there are 15 bearings to supply 805 million tonnes of raw materials.

Paleozoikum Železných hor – East Bohemia

This area in which there is the occurrence of crystalline limestone is situated in the middle of Železné hory. Here we can register the occurrence of limestone containing approximately 95% $CaCO_3$ and darker crystalline limestone with lower levels of carbonate (90% $CaCO_3$). Limestone is used for calcinations in mined lime kilns. Sub-sieved fraction of limestone of poorer quality is used as raw material for the manufacturing of portland slink in the cement industry in Prachovicích. The local stocks have been calculated to be 170 million tonnes.

Středočeské metamorfované ostrovy

Crystalline limestone is found in two small isolated areas and it considered to be of good quality. Due to mining, Sedlcany Skoupý limestone is finely grounded and added to the fertilization of land used for agriculture, and can also be used to produce animal feed.
Limestone suspension is used in sewage treatment plants, and in the desulphurization processes of flue gases. Another use for ground limestone is the manufacture of a mixture of asphalt for road surfaces. Total reserves have been calculated at 40 million tonnes.

Krkonošsko-jizerské krystalinikum

Crystalline limestone, strongly metamorphosed, apparently from the Devonian age, occurs in several areas. It is often dolomitic limestone, with a high content of silicates. Total reserves have been calculated at 552 million tonnes.

Moldanubikum southern Bohemia

In the diversified group of Moldanubian, there are 24 bearings of strongly metamorphosed crystalline limestone. Given its strongly dolomitic characteristic, in the past, it could not be used for the production of cement. Total deposits are held at 461 million tonnes.

Moravský devon

Limestone is mostly from theDevonian age, partly from the Precarboniferous age. Basically, the most important limestones are the following: Vilémov limestone, Křtinský limestone, Hádský and also Lažánecký limestone. Sedimentary limestone, dominated by the biomicrit types are present, as well as biolitic limestone and sandy limestone. Their diagenetic conversion is stronger than in the Barrandienský limestone, creating weak points of metamorphosis. Vilémovic limestone has a high content of $CaCO_3$, approximately 96-98%. High-quality “křtinský” limestone is extracted in wet carry. It is used for the manufacture of Class I lime and limestone and the one with less carbonate content is used for the manufacture of portland cement. A major plant is the cement factory in Hranice. Total reserves in 245 deposits are 461 million tons.

Silesikum - Branná group, Vitošov region and a series of zábřežská

In this area there is less bearing crystalline limestone, forming a lens zone in heavily metamorphosed rocks, some of them benefiting from a high limestone content which can go up to 98% $CaCO_3$. The Lipová deposit is one of the cleanest limestones across the country. Crystalline limestone is used for noble stone mason production, and was later re-

used as filler. Therefore, Lipová's site produces micro grinded limestone. In the Vitošov deposit, the raw limestone is extracted and in Měrotín it is grinded to lime and limestone. In Silesiku there are 8 bearings with stocks of 147 million tonnes of raw materials.

Silesikum – skupina Branné, oblast Vitošov a zábřežská série

It is possible to find limestone with clay contents of 60-80% in larger and medium-sized deposits. Sediments with a high content of clay are also called hard, and are particularly suited for the production of portland cement. The limestone is extracted for cement factories in Čížkovice and in Lovosice. Hard limestone, with lower carbonate content, is calcinated to hydraulic lime. Today is successfully used for flue gas desulphurization. Bearings stocks are about 493 million tonnes.

Česká křídová pánev (uherská a kolínská oblast)

In this area, sedimentary limestone from Jurassic age can be found, forming the calcary reefs. There is clean raw material, namely limestone and clay, with average percentages of $CaCO_3$ which vary between 95%-97%, extracted. The cement plant at Štramberk that processed the unsieved fraction for portland cement ceased production of cement and currently produces ground limestone for WFGD. Stocks have been calculated at 470 million tonnes.

The position of those sites is shown on the overview map of the Czech Republic, as shown in Figure 15

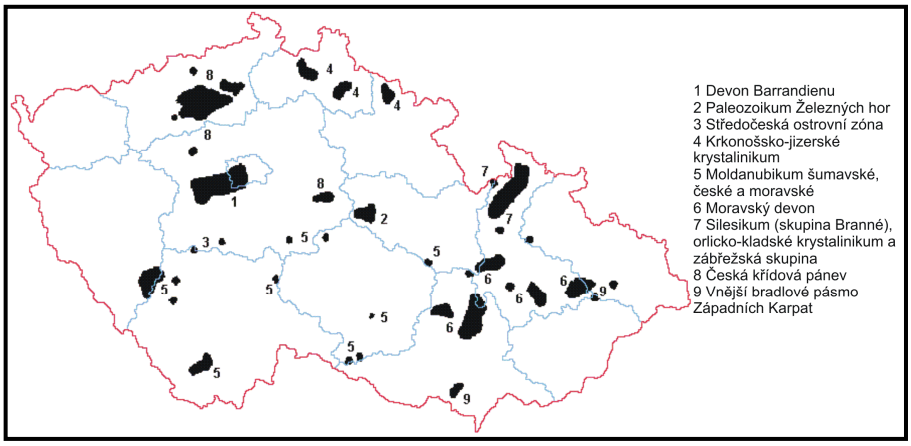

Figure 15 – Limestone mining sites in the Czech Republic.[40]

As the following table illustrates, since 1988, mining limestone in the Czech Republic and the decline registered in the year 1997 which shows a 32% decrease. This is a sharp decrease in the use of cement, lime, ground limestone and grades the increased efficiency in the context of the new market conditions, including the exports. The data from the Association of Cement and Lime Producers of Bohemia, Moravia and Silesia is clear about another important fact which is that high content limestone mining declined in about 40%. This illustrates the diligence with which it is governed by a complex use of bearings.

Table 16 – Limestone mining in the Czech Republic.[7,40]

Mining in thousands. T	1988	1997	1999	2000	2001	2002	2003
Limestone with high content of $CaCO_3$	7 552	4 536	4 673	4 784	5 071	5 017	4 573
Other limestone	8 737	6 474	6 705	6 592	5 452	4 854	5 663
Total	16 289	11 010	11 378	11 376	10 523	9 871	10 236

The Czech Republic has a relatively large stock of limestone. According to data evaluation on 2003 stocks, there were about 4.5 billion tons. [40] By putting in the number of current consumption rates, it is found that the limestone stocks have a life of approximately 450 years. After 1997, limestone consumption increased due to desulphurization processes, but this increase was offset by a decrease in its consumption for the production of building materials. In the 21st century, all evaluations are calculated on the increased consumption of limestone for desulphurization purposes, although only during a few decades because it is clear that the time has come for the end of coal burning for electricity generation; the evaluation also counts on a significant drop in consumption of raw materials for the production of building materials. Such a trend would have extended the life of stocks, contribute towards the of protection of the landscape and local flora.[7]

Finely ground limestone is currently an essential raw material for FGD systems. The exhaust gases resulting from the burning of brown coal, in particular for power and heating, as well as the incineration of waste, uses a large number of desulphurization methods, in which limestone or lime appears as a basic absorbent.

For a small or medium-sized boiler it is not financially viable to build a costly desulphurization unit. In this case, to reduce emissions of SO_2, it is more cost-effective to add additives to the coal, i.e., add ground limestone to the coal prior to its incineration in the combustion chamber.

Consumption of lime and limestone for desulphurization processes, according to statistics from the Research Institute for the Protection of the Environment in the Czech Republic, is rising rapidly, as evidenced by Tables 17 and 18.

Table 17 – Consumption of lime for the protection of the environment. [7]

lime [k. t]	Prognostic in 1997					
	1995	1996	1997	1998	1999	2000
Lime for desulphurization	0	20	70	120	125	144
Lime to other sectors of the environment	50	50	40	60	70	86
Lime for the environment – Total	**50**	**70**	**110**	**180**	**195**	**230**

Table 18 – Limestone consumption for the protection of the environment. [7]

limestone [k. t]	Prognostic in 1997					
	1995	1996	1997	1998	1999	2000
Grossly grinded limestone for wet scrubbing	130	400	610	885	1080	1050
Minced limestone for wet scrubbing fluid and desulphurization	10	115	325	625	885	1025
limestone for the environment - Total	140	515	935	1510	1965	2075

2.6.3 Limestone dissolution and SO_2 absorption

Solubility of limestone in water is relatively low. Between 17ºC and 25 ° C it is 14-15 $mg.dm^{-3}$ At 100℃, it reaches about 30-40 $mg.dm^{-3}$. [14] In the presence of CO_2, the solubility of the limestone increases with the growing pressure of CO_2, as shown in Figure 16.

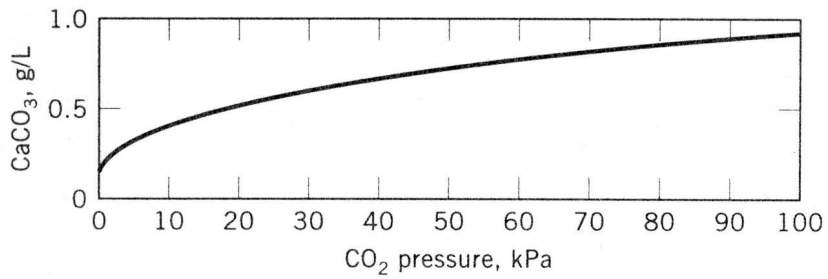

Figure 16 – Limestone solubility according to CO_2 pressure.[14]

The absorption of SO_2 into limestone slurry can include the following diffusion and dissociation reactions:

$SO_2(g)$ Gas-liquid diffusion	(Diffusion)	(31)
$SO_2(g) \leftrightarrow SO_2(aq)$	(Dissolution)	(32)
$SO_2(aq) + H_2O \leftrightarrow H_2SO_3$	(Dissociation)	(33)
$H_2SO_3 \leftrightarrow H^+ + HSO_3^-$	(Dissociation)	(34)
$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$	(Dissociation)	(35)
$CaCO_3(s) \leftrightarrow CaCO_3(aq)$	(Dissolution)	(36)
$CaCO_3(aq) \leftrightarrow Ca^{2+} + CO_3^{2-}$	(Dissociation)	(37)
$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$	(Dissociation)	(38)
$H^+ + HCO_3^- \leftrightarrow CO_2 + H_2O$	(Dissociation)	(39)

As well as the ongoing diffusion of dissolved chemical individuals in the liquid film and, the reactions between them:

$SO_2 + HCO_3^- \leftrightarrow HSO_3^- + CO_2$	(Reaction)	(40)
$SO_2 + SO_3^{2-} + H_2O \leftrightarrow 2HSO_3^-$	(Reaction)	(41)
$CO_3^{2-} + HSO_3^- \leftrightarrow HCO_3^- + SO_3^{2-}$	(Reaction)	(42)

Sulphur dioxide diffuses over the gas-liquid interphase and dissolves into the liquid and diffuses, while, simultaneously, the limestone dissolves and also dissociates. Then, the reaction between formed sulphite and carbonate ions occurs according to equations 40-42. [32]

The degree of dissociation depends on the pH of absorption suspension, as shown in Figure 17.

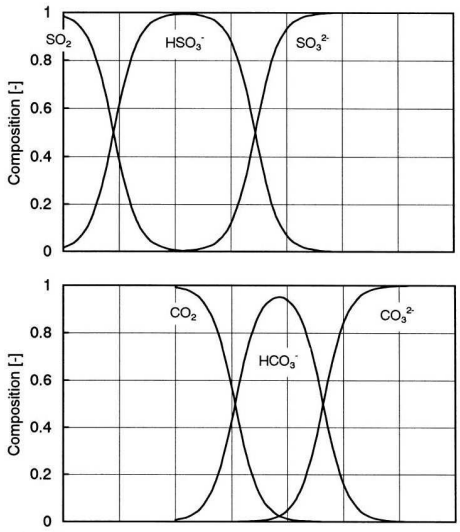

Figure 17 – Dissociation degree of absorption suspension.

Figure 18 shows a concentration profile of the gas-liquid phase.

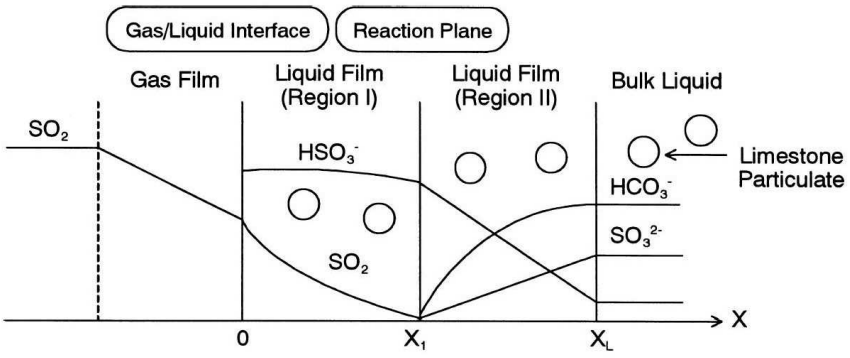

Figure 18 – Sulphur dioxide absorption profile during the gas-liquid phase.[32]

The picture illustrates that the sulphur dioxide dissolved in the liquid film reacts (reactions 40 and 41) and is consumed during the emergence of the hydrogen sulphide ion. In the X axis, when the entire sulphur dioxide reacts, the predominant reaction will start to establish a balance in the liquid phase.

During the liquid-solid phase, as illustrated in Figure 19, the product of reaction 38 is consumed, the carbonate ion is released and then consumed to produce hydrogen carbonate. Due to this, we can state that the H^+ ions are major players affecting the dissolution speed of limestone.

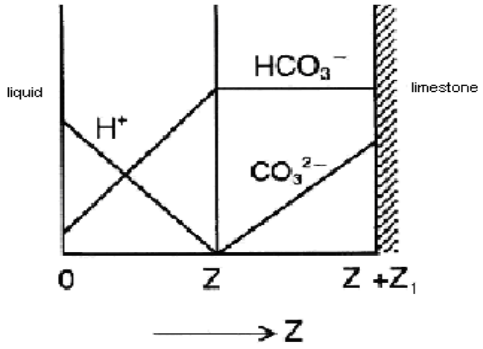

Figure 19 – Concentration profile during liquid-solid phase [32]

Another key parameter affecting the dissolution speed of limestone is the size of the liquid-solid interphase area, which is linked to the particle surface or mild grinding limestone.

The limestone's dissolution reaction rate can be expressed in equation 43: [1]

$$\frac{d[CaCO_3]}{dt} = k.([H^+] - [H^+]_{eq}).S_{sp}.[CaCO_3] \qquad (43)$$

$[CaCO_3]$	carbonate concentration in suspension	[mol.dm^{-3}]
$[H^+]$	the concentration of hydrogen ions	[mol.dm^{-3}]
$[H^+]_{eq}$	equilibrium concentration of hydrogen ions	[mol.dm^{-3}]
S_{sp}	specific surface of carbonate in the suspension	[m^2.g]

Figure 20 shows the dissolution rate of limestone in various pH and various pressures of CO_2.

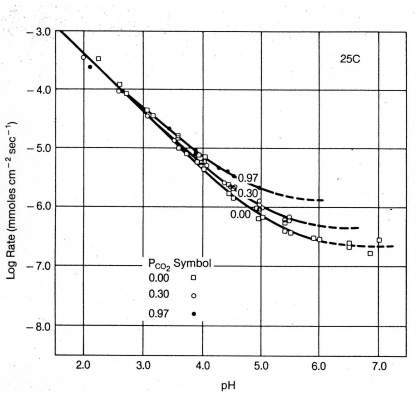

Figure 20 – Limestone dissolution speed at various pH and CO_2 out pressure [atm] [1]

The modulation of the pH effect on the kinetics calcite dissolution [3] in Figure 21 shows that in different intervals of pH, the dissolution speed is affected by particles' surface. With pH ranging from 2-5, and the dissolution is affected by the adsorption of H^+ ions (curve 1), with pH from 5-8, speed is affected by the adsorption of HCO_3^- ions (curve 2); with pH higher than 10, the speed is affected by the adsorption of OH^- ions for the creation of Ca(OH) particles (curve 3) and particulate $CaOHCO_3$ (curve 4). Curve 5, the total specific speed dissolution, is a result of the model.

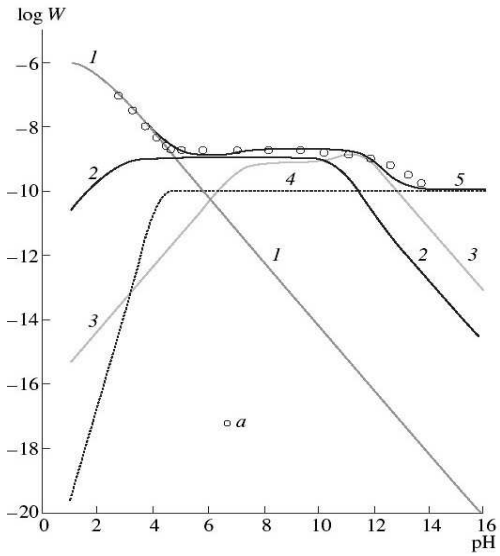

Figure 21 – pH dependence of calcite speed dissolution [3]

The speed of limestone dissolution may also be affected by CO_2 mass transport over the gas-liquid interphase;

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad (44)$$

The effect of the intensity of stirring influences the dissolution of limestone. This effect was studied in an acidic environment (HCl solution), in a simple reactor with a paddle mixer (the results of the experiment show that the dissolution process depends on the rotational speed of blades). [24]

In the first phase, limestone dissolves very quickly according to reaction 45 and after the exhaustion of H^+ ions, reaction 46 starts to be very slow. The fact that the second phase of dissolution of limestone is dependent on the intensity of mixing, allows us to conclude that the transportation of CO_2 over the interphase the gas-liquid is of vital importance.

$$CaCO_3(aq) + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \quad (45)$$

$$CaCO_3(aq) + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (46)$$

2.6.4 Gypsum

The final product from the FGD is a suspension removed from the hydrocyclone, where the ratio of 1:1 (about 50% water and 50% gypsum) is concentrated. The water at the top of the hydrocyclone is returned to the process (it contains more or less 1% to 2% of limestone), while the concentrated part at the bottom is then drained on the belt or drum filter, which deprives it from water and gradually washes the first $CaSO_4.2H_2O$ which contains from 12% to 20% humidity. Alternatively, $CaSO_4.2H_2O$ can be thickened in centrifuges. The moisture content of drained product varies between 6% to 8%. Dewatered gypsum can be further processed for building materials, or used as a regulator in the hardening of cement. Should it not be reused for sales, it can be stabilized and taken to a landfill. [34]

2.6.4.1 *Gypsum establishment*

Once the liquid phase calcium sulphate has decongested, it will start to crash as dihydrate calcium sulphate (gypsum) (solubility of $CaSO_4.2H_2O$ is 2.4 $g.dm^{-3}$ at 65℃ [5]). Figure 22 shows two regimes in which the clotting of gypsum may occur: the growth of crystals and the creation of crystallization nuclei. The relative saturation of 1.3 to 1.4 outweighs the creation of small crystallization nuclei, which incrustates on the absorber surface. If the suspension is maintained with an adequate amount of gypsum particles, the growth of crystals is suppressed and incrustation does not take place. [19]

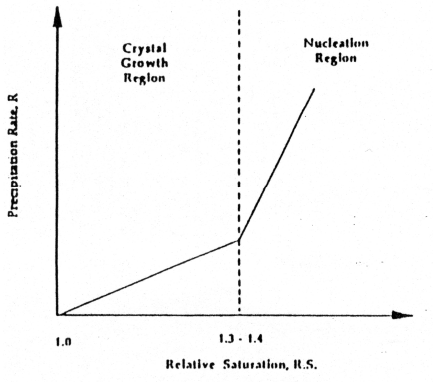

Figure 22 – Gypsum precipitation according to relative saturation.[19]

The ratio between L/G and concentrations $CaSO_4.2H_2O$ depends on the value of the degree of saturation of the suspension. The optimum value of L/G ratio in non-additivated suspensions varies between 10 to 30 $dm^3.m_N^{-3}$. [34]

2.6.4.2 Destination of gypsum

Pure gypsum is a valuable material for the construction industry. It is used as a stabilizer in the hardening of cement in the amount of approximately 3 to 4% wt. and in plaster building materials such as gypsum plasters, gypsum board material (plasterboard), floors and car parks as substitute for concrete substructure.

The composition of gypsum and natural gypsum are compared in Table 19. [35]

Table 19 – Composition of industrial and natural gypsum [35]

	Natural gypsum	**Gypsum**
Humidity	1	7-10
$CaSO_4.2H_2O$	78-95	98-99
Cl	<0,001	<0,01
Na_2O	0,02	<0,01
MgO	-	<0,01
Fe	-	<0,05
F	-	<0,05
SO_2	-	<0,05
CO_2	-	1
K_2O	-	0,5
pH	6-7	5-8
Inerts	5-20	-

2.6.5 Action additives

To increase the effectiveness of wet limestone methods, additives are included into absorption suspension. These additives can be organic or inorganic. An additive is a substance that is added, in a low concentration, to the desulphurization system to improve the absorption capacity of the scrubbing suspension, which leads to savings in investment and operating costs and/or improvement of efficiency and performance of equipment.

During the absorption of SO_2 into the absorption liquid, an acid that is continuously neutralized by limestone dissolution is continuously being formed. Neutralization speed significantly affects SO_2 absorption in limestone suspension. The Na^+ and Ca^{2+} ion used as additives increase the alkalinity of limestone liquid in the form of SO_3^{2-} ion. If there is enough of this ion in the liquid, the balance of reaction sulphite-bisulphite shifts the pH of scrubbing liquid, so that the neutralization of SO_2 absorbed takes place quickly, hence making SO_2 absorption from the gas faster. The process is limited by the resistance against the transfer of SO_2 into gaseous phase. Since the restriction lies in the speed with which SO_2 can be absorbed from the gas phase, for the desulphurization process the contact with the surface of the liquid gas is important. Therefore, the value of L/G in these systems is maintained at high values, for example, 20-30 $dm^3.m^{-3}$. The speed with which the solid phase dissolves limits the neutralization of absorbed SO_2, and hence becomes a limiting step. It is not unusual that the suspension entering the absorber with a 5.5 pH leaves it with a 3.5 pH. The more the pH falls, the more the partial pressure of SO_2 rises in the suspension, thereby limiting the absorption force of SO_2 into the suspension. Therefore, the decreases in the pH effect are suppressed by the large stream of liquid and also by the necessary amount of Ca^{2+} ion in absorber. [19,33,34]

2.6.5.1 *Organic additives*

Flue gas desulphurization cost and performance are becoming increasingly important as limitation ceilings are becoming more severe. Operators of coal-fired boilers need FGD systems that are reliable and based on proven technology.

The effectiveness of flue gas desulphurization using suspension of limestone can be enhanced by using appropriate organic additives. The organic acids used have to have a constant dissociation in which the value varies between the value of the constant dissociations of the carbonate acid and bisulphite. Their common feature is that they constitute soluble calcium salts, which increase the alkalinity of soluble suspensions.

Increasing the efficiency of desulphurization using organic acids is dependent on a number of factors, such as the transfer of materials inside the absorber without the presence of additives, working pH, sulphur content of coal, buffer capacity of a particular concentration of organic acids. [19]

Organic acids, as effective absorbers, allow the pH range of equilibrium reactions between particles. The importance lies in the fact that the removal of SO_2 is not so

dependent on sorbent's alkalinity, therefore L/G ratio can be lower. The advantage of organic acids is their low sensitivity to the content of chlorine and fluorine in the exhaust gas. This makes it possible to carry out the process of absorption and cooling combustion gases in a single system, with a single circulation circuit. [25,34]. Literature used for our research shows that most of acidity should range between 0> x ≤ 7 mmol/l. When using adipic acid in the concentration of 3 mmol/l, this increases desulphurization efficiency in 83% to 90% and the level of residual limestone is reduced from 4,6% to 1,4 wt%. [6]

2.6.5.1.1 Organic acid

Organic dicarboxylic acids significantly improve the removal of sulphur dioxide in two ways. First, the diacarboxylic acids improve the dissolution rate of limestone into the liquid slurry feed to the scrubber. Secondly, the mass transfer rate of SO_2, from the gas phase to the scrubber liquid, which is often a limiting factor in scrubber systems, is improved.

2.6.5.1.2 The action of organic acids

The action of organic acids is illustrated on the Figure 23.

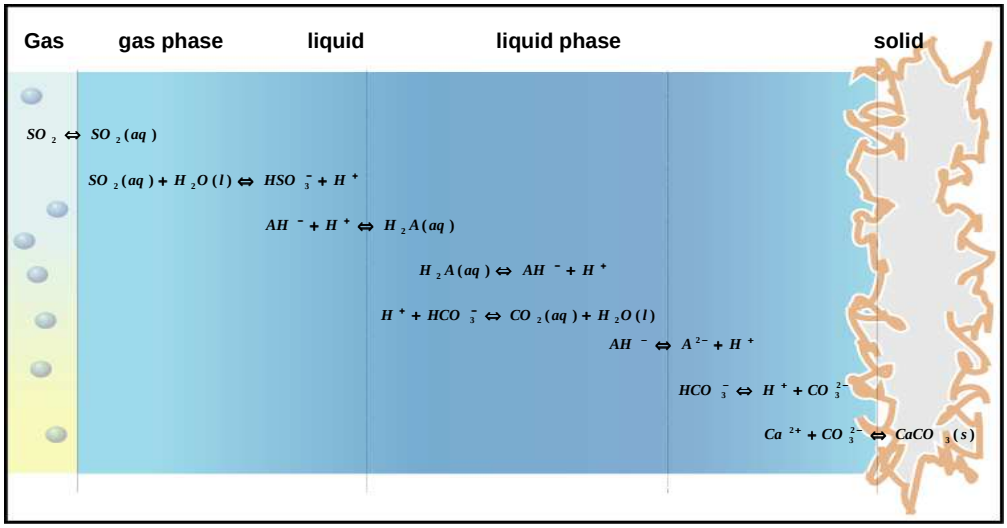

Figure 23 – Action mechanism of dicarboxylic acids [6]

Organic acids can be seen as vapour-liquid mass transfer enhancing effect.

Rapid mass transfer of SO_2 from the vapour phase to the liquid phase is critical for effective SO_2 scrubbing. Once the surface of a scrubbing droplet is saturated with SO_2, no more SO_2 can dissolve, even if the bulk liquid has not yet reached saturation levels. Dissolving can continue as SO_2 diffuses away from the surface into the bulk liquid (relatively slow), or if the concentration of SO_2 at the surface of the liquid droplet can be minimised in other ways, such as through chemical reactions (relatively fast compared with SO_2 diffusion). This can be accomplished by the buffer effect of the added acid, which consumes the acidity generated by SO_2 as it dissolves, converting SO_2 into sulphite salts.

Organic acids can also be seen as solid-liquid mass transfer enhanced by additives, which improve the limestone utilization. It reduces the limestone consumption by allowing the operation of the scrubber at a lower pH than would otherwise be possible. Generally, high pH is desirable for maximum SO_2 absorption (better acidity neutralization), but low pH is desirable for a maximum rate of limestone dissolving. If a scrubber must be run at high pH because limestone is not used completely, through their buffering action, organic additives improve SO_2 absorption at lower pH. Operation at lower pH reduces limestone consumption by improving limestone dissolution, thus enabling more complete utilization of limestone in the process. This effect is very important for the desulphurization process.

2.6.6 Consumption and the economics of additives

The quantities of additives used in wet limestone technology depend on desulphurization efficiency and its loss in the system. Losses of additives include the chemical degradation (decarboxylation) in the process of desulphurization, removal of calcium sulphate, evaporation at temperatures prevailing in the absorber. Losses are also due to the volatility of additives. For example: formic and acetic acid certainly have greater volatility than the longer chain acids. Further losses are caused by the draining of moisture, which is taken from process during the thickening of gypsum. In the U.S.A., the investment costs for the installation of equipment for the application of additives for large power plants is estimated to cost approximately 100 000 to 300 000 USD. This equipment includes the reservoir for additives which, according to the type of additives, may require heating of pumps and pipes leading into the pit absorber. For a block of 600MW fired by coal with a sulphur content of 2.6% and a concentration of 500 ppm, with the additives in the purifying circuit and without regeneration, the scouring device can be estimated about 75 000 to

100 000 USD. In fact, the total cost of the additive is lower than expected as it would have to increase the consumption of limestone with the required grain size to achieve higher desulphurization efficiency. The investment required for the additive system is approximately 1% higher than in non-additived systems and operating costs will increase by 1% to 2%. [19]

2.6.7 Degradation of additives

The speed of degradation of adipic acid was examined [2], in the pilot plant. Tests were carried out considering two modifications: the first consisted in using the absorption suspension of limestone with distilled water and flue gases from the combustion of natural gas; the second implied the use of liquid from a real suspension (mixed with fresh lime) from the industrial desulphurization unit with coal combustion.

The mechanism of the chemical degradation of the situation proposed [26] consists in the oxidation of conjugated carboxylic acids, which are likely to take place with the complicity of free radicals generated during the oxidation of HSO^{-3} ion [12]. These describe the degradation of adipic acid either combined with oxidation (eg Adipic => Glutaric => succinic…), or with oxidation decarboxilation (eg Adipic => valeric => Butanoic acid…) for the formation of alkenes and carbon dioxide. The products of both mechanisms, in addition to oxalic acid, are found in the suspension. Absence of oxalic acid can be caused by the rapid dissolution of the carbon dioxide. In addition, the possibility of making organic substances with longer chains (than six carbon atoms) is also implied.

Degradation adipic acid also depends on temperature and pH suspension. At 32℃ a constant degradation speed of adipic acid was measured, 0,15 ± 0,1 day^{-1} for 42℃ 0,2 ± 0,1 day^{-1} , and at 50℃ 0,55 ± 0,1 days $^{-1}$, which is almost four times more than the 32℃. Reducing the pH from 5,4 to 4,7, with a drop speed of constant degradation of adipic acid from 0,55 ± 0,1 day^{-1} to 0,4 ± 0,1 day^{-1}, it is clear that the degradation of adipic acid decreases when temperatures drop and pH diminishes (see Figure 24).[2]

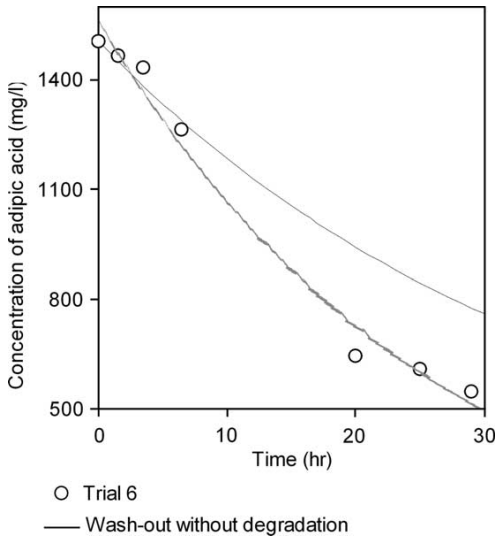

Figure 24 – Adipidic acid degradation.[2]

It was found that increasing concentrations of trace elements inhibits the chloro-chemical degradation of adipic acid (see Figure 25).[2].

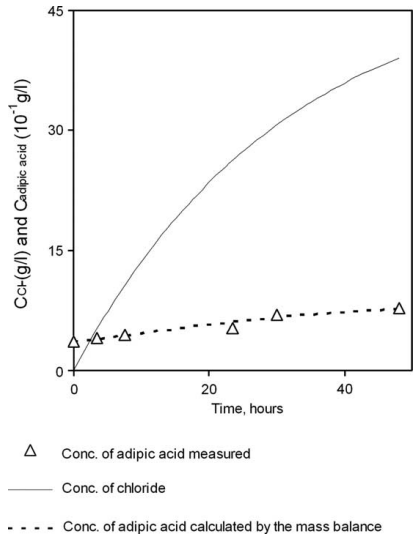

Figure 25 – Inhibition of adipic acid decomposition by chloridic acid [2]

Both suspensions (see above) [2] have been tested for biological activity. The test samples were made for each suspension to which adipic acid was added and then divided into two parts. The first half was heated at 140℃ during 45 minutes to analyse the eradication of microorganisms. The second half was not heated. After placing the samples in the incubator during 1, 3, 7 and 14 days, was analysed their reaction and it revealed that the biological activity contributes to the degradation of adipic acid only in the event of a

suspension of an industrial desulphurization unit. [2]. It is very significant that after 3 days there was 70% concentration and after 7 days only 30%.

2.6.8 The influence of additives on the operation

Additives for the removal of SO_2 increases efficiency and reduces operating costs. The new device can be applied in the designing of smaller absorber dimensions and thus lowering acquisition costs. For existing facilities, the effect can be as follows: [19]

• increasing the effectiveness of the device. At the same value of L/G, there is an increase in efficiency. For example, the burning of coal with a sulphur content of 2.6%, after the addition of potassium formate in the amount of 500 ppm, increased the efficiency of desulphurization from 90% to 96%. Therefore, in this case, it was possible to reduce L/G by half for the same desulphurization efficiency.

• pH change. Organic acid acts on the suspension producing a buffer effect. The use of additives can achieve the same desulphurization efficiency at lower pH with greater use of limestone.

• Reducing the cost of grinding limestone. Grinding limestone is a high energy demanding. For example: reduce the milling from 95% to 75% below 44 μm saves half the electricity required for grinding. Reducing the pH, which occurs as a result of the addition of additives, improving the use of limestone added for the same desulphurization efficiency. Therefore, with the use of additives the limestone used can be grossly grinded.

• Reducing the creation of scaling in washing machines and drop precipitators. The addition of soluble organic acids increases alkalinity which makes the limestone absorbent during a longer time. Positive applies when as a result of low pH (under 5) and a high content of fluorine in the exhaust gas, F^- ion reacts with aluminium from the ash for the creation of an AlF_6^{3-} ion, which blocks the dissolution of limestone and raises the creation of scaling.

• Ability to act positively in increasing concentrations of SO_2. Since the organic acids have buffer capacity, the system is less sensitive to the change in the concentration of SO_2 compared to the situation in which the dissolution of limestone in the scrubber was a limiting step. For example, increasing concentrations of SO_2 in the flue gas from 2000 to 4000 ppm in non-additived process decreased the efficiency from 90% to 84% and thereby increased emissions from 200 ppm to 640 ppm.

• Reducing sensitivity to the process by increasing the concentration of chloride. Chloride particles under normal conditions worsen the dissolution of limestone, due to an increase in levels of soluble calcium and relative saturation of calcium carbonate. The use of additives requires an alkalinity liquid phase provided the effects of additives and therefore removal of sulphur dioxide, is not strictly dependent only on the dissolution of limestone. In the case of increasing the concentration of chloride ions from 10 000 ppm to 50 000 ppm, the desulphurization efficiency is decreased from 94% to 79%.

2.6.9 Additives used to inhibit the oxidation of sulphites

Gypsum incrustation is the result of oxidation chemistry which has not been fully completed, or of the characteristics of the growth of crystals. These incrustations have very little to do with structural deficiencies. In the U.S.A., there are many systems operating under conditions where the rate of oxidation very effectively inhibited thiosulphate formation. Thiosulphate interferes with the promotion of oxidation, and sulphite radicals react with it, thereby inhibiting the oxidation of sulphite. An improvement of this method is a combination of a complexing agent, such as EDTA, in very small doses. Sulphite radicals, which react with thiosulphate particles, are considered to be the result of reaction sulphite ions with trace elements. EDTA binds trace elements that are dissolved in the scrubber thereby effectively blocking initial reaction in which sulphite particles are produced.[19]

2.7 Limestone suspension with the use of additives

The limestone suspension can include additives which affect, either positively or negatively, the absorption capacity. As the calcium sulphite and gypsum are formed due to relative saturation, the limestone dissolves due to its relative saturation. Therefore, when decreasing the concentration of calcium and (or) carbonate ions in the solution, the limestone dissolves more quickly. A forced oxidation (aeration of the suspension) may increase the dissolution speed of limestone versus unintentional oxidation. In the case of inhibited oxidation, during which the concentration of dissolved sulphate is reduced, the concentration of calcium ions and relative saturation of calcium carbonate in the suspension are also lower. While inhibited oxidation reduces the concentration of dissolved calcium, controlled oxidation reduces the carbonate ions concentration in the solution. In this case, oxidizing air is added to the suspension, in the absorber, for the

striping of CO_2 from the solution. This leads to a reduction in the concentration of carbonate ions to a relative saturation of calcium carbonate, which causes rapid dissolution of limestone. [19]

The addition of magnesium may have the opposite effect on the limestone dissolution; it might increase the concentration of sulphite ions in equation 44. Higher levels of soluble sulphites have a "blinding" effect on limestone particles. So, while on the one hand, the addition of magnesium in the wet limestone increases the degree of flue gas desulphurization, on the other hand it also reduces the use of limestone.[19]

3 Experimental framework

In the experimental part the analytical methods, devices and samples used are described. Further on experiments are made to obtain information about the behaviour of the samples used. For the different types of experiments is presented a description of each device, the measurement procedure and the discussion of the results.

3.1 Analytical methods and devices used

This chapter describes the equipment [27,15,11,36,43] and technical data used in the experiments.[18]

3.1.1 SO_2 analyser Servomex Xentra 4900

This online analyser includes two channels for measuring the concentrations of SO_2, which operate based on the infrared absorption spectrometry and use gas filter correlation. The measurement range of the instrument is from 0 to 3300 ppm of SO_2 with the error of 1% of the measured value of at least 5 ppm.

3.1.2 X-ray fluorescence analysis of solids

With this method it is possible to get information about elemental composition of the sample material. The method is applied mainly to solid samples all prepared using different techniques (grinding and polishing, pressing, melting).

X-ray fluorescence is the characteristic emission of secondary X- rays of the material that was excited with high-energy X-rays.
The term fluorescence is applied to a phenomenon in which the absorption of higher-energy radiation results in the re-emission of lower-energy radiation.

3.1.2.1 *X-ray spectrometer ARL XP 9400 +*

It is a sequence (it has an adjustable monochromator) of dispersed waves (it uses the waves properties of X-ray radiation). Qualitative and quantitative information about elements is then obtained in the spectrometer. It can analyse materials and compact powder samples (measurement takes place in a vacuum).

Equipment description:

• X-ray lamp with **Rh**-anode with **Be** front window with a source of X-ray lamp at the maximum wattage 3.6 kW,

• goniometer with a fully automatic 4-position primary alternator collimator (0.15, 0.25, 0.6 and 2.6 of the angular admittance) and 9-position changed crystals, which is equipped with 6-plane crystals LiF200, LiF220 , Ge111, PET, TLAP and AX20,

• two detectors – proportional flow (works on the principle of ionization of gas with X-ray radiation detection, the rate depends on radiation energy) and scintillation (based on the excitation of electrons due to the impact of radiation on crystal NaCI with activated thallium resulting in the production of light measured on photomultiplier).

3.1.3 Laser granulometry

Measurement of particle size distribution is based on the principle of laser diffraction. Laser diffraction is a method, which uses the scattering of light after the impact of the particle. The angle of dispersion is indirectly proportional to the size of particles, which leads to dissipation. The concept of dispersion of light is generally defined as a reflection, breaking and bending of light. Alterations of this track are recorded by ray detector, which handles the incident rays.

3.1.3.1 *Laser particle size analyzer - Analysette 22 ®*

The device that works based on the above mentioned principle (from the manufacturer Fritsch, Idar-Oberstein, Germany) uses a helium-neon laser. Measuring suspension circulates on the entire sample and the reflected rays are recorded on a photodetector.

3.1.4 The measurement of the specific surface using BET

The measurement of solids specific surface serves a wide range of physical methods, based on interaction with the surrounding environment. Most of them are sorption methods using gas to the surface. One of the best and most popular model is adsorption on the surface of solid substances derived from Brunauerem, Emmetem and Tellerem (BET). Using this model, sample quantities are adsorbed at different pressures to calculate the surface size. Although, different authors defend several basic assumptions:

• There is no mutual interaction between molecules in absorption layers,
• Adsorption heat of the first layer is higher than that of other layers.

3.1.4.1 *Coulter SA 3100*

Instrument that measures inner surface pores size, and its distribution. Measurements are made by adsorption of nitrogen at -196℃. The absor bed quantities are measured by static volumetric method based on the measurement of the pressure of nitrogen gas in a container (which volume is known).

3.2 Limestone and pure calcium carbonate samples and their characteristics

The choice of limestone and $CaCO_3$ samples was based on the assumption of their potential and practical application in the Czech power. Two samples were used for suspension as described below.

Basic suspension material was chosen, limestone from Devon-Barrandian - Čerstovy schody, suitable for use in environmental purposes due to its high purity. This material was supplied by Melnik power station; it is used as raw material of WFGD.
This material was wet grinded in porcelain spherical mill with alumina balls for 12 hours. Afterwards the sample granulometry was measured.
The comparative sample chosen was pure calcium carbonate (prepared by precipitation). The manufacturer is Lachema Neratovice.
In Figures 26 and 27 granulometric cumulative curve (1) and distribution, curve (2) are presented.

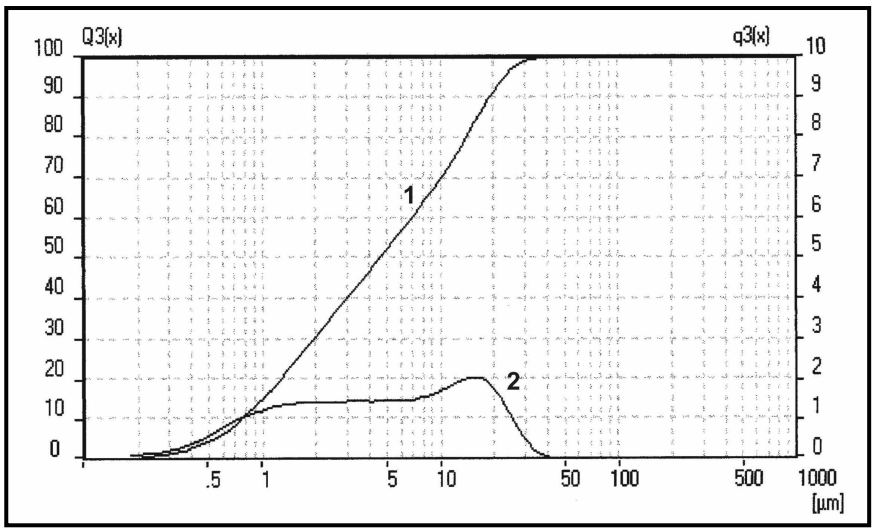

Figure 26 – Granulometric analysis of grinded limestone Čertovy schody.

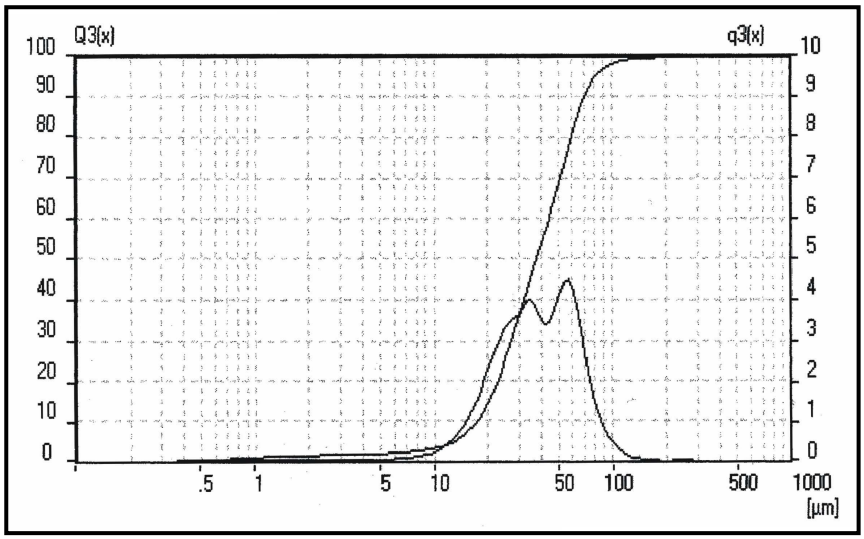

Figure 27 – Granulometric analysis of pure $CaCO_3$.

Table 20 – Granulometric analysis of limestone and pure $CaCO_3$.

Sample	Part of sample under certain size in [%]				Median [µm]	Mode[µm]
	<10µm	<20µm	<40µm	<100µm		
Limestone Čertovy schody	5	91,5	99,9	100	4,56	15,49
$CaCO_3$	3,3	14,5	54,1	98,3	37,34	34,1

The table 20 shows that the Čertovy schody's limestone has the majority of particles below 40 μm while pure $CaCO_3$ below 100 μm. With the aim of achieving comparable parameters, the pure $CaCO_3$ was grinded in the same way as the limestone, see on figure 28 and table 21.

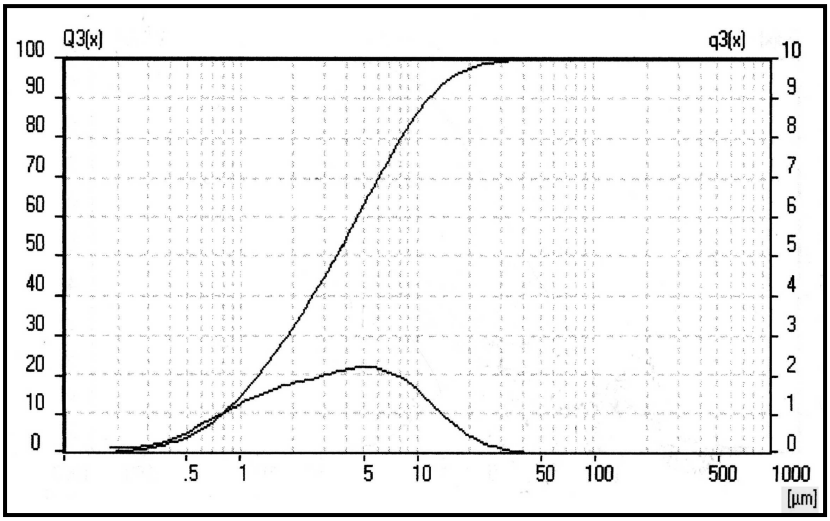

Figure 28 – Granulometric analysis of grinded pure $CaCO_3$

Table 21 – Granulometric results from grinded pure $CaCO_3$

Sample	Part of sample under certain size in [%]				Median [μm]	Mode[μm]
	<10μm	<20μm	<40μm	<100μm		
Pulverized $CaCO_3$	86,3	97,8	99,9	100,0	3,48	5,13

Specific surface areas of absorbents samples were measured (BET) on the instrument Coulter SA 3100, including the volume of pores; the obtained values are presented in the table 22.

Table 22 – Samples BET surface and pores volume.

Sample	BET surface [m^2.g]	Pore volume [ml.g]
Čertovy schody's limestone	2,061	0,0092
Pure $CaCO_3$	0,063	0,0022

In the table it can be seen a large difference in surface samples Čertovy schody's limestone and pure $CaCO_3$.

Elemental composition of the samples was obtained by X-ray fluorescence analysis.
The representation of the main components of limestone is summarized on table 23.

Table 23 - Čertovy Schody limestone and pure $CaCO_3$ composition

Element	Čertovy schody's limestone [wt%]	pure $CaCO_3$ [wt%]
$CaCO_3$	97,72	99,76
MgO	0,391	0,107
SO_3	-	0,100
Al_2O_3	0,447	-
SiO_2	1,07	-
Fe_2O_3	0,131	-
K_2O	0,022	-
TiO_2	0,017	-
MnO	0,014	0,016

3.3 The additives (organic acids)

A number of organic acids came into consideration, mainly those that are characterized by relative low price, low volatility and high stability in the desulphurization system. Furthermore, the use of organic acids, or a mixture of organic acids, should not created problems with waste water from the desulphurization unit.

A list of selected and tested organic acids and their properties are presented in table 24.

In order to assume proper functionality, the acids need to have a buffer effect of dissociation constants in the range of sulphuric and carbonic acid (which are present in the scrubbing solution). Another prerequisite is the solubility of the calcium salt or low-value of stability of the formed complexes.

Calcium ions tend to form large complexes with tricarboxylic acids and smaller complexes with monocarboxylic acids. [8]

Table 24 – Characteristics of organic acids [14,5,17,8]

Acid	Molecular Formula	M_r [g/mol]	calcium salts solubility in water [g/l]			[log K] 25℃	Dissociation constant pK_a (for t=25℃)			
							pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
Formic	CH_2O_2	46,03	(20℃) 166	(50℃) 173	(90℃) 182		3,75			
Acetic	$C_2H_4O_2$	60,05	(20℃) 347	(50℃) 328	(90℃) 302	0,53	4,75			
Propionic	$C_3H_6O_2$	74,08				0,50	4,87			
Oxalic	$C_2H_6O_2$	90,04	(18℃) 0,006	(50℃) 0,0096	(95℃) 0,0145	3,1	1,23	4,19		
Malonic	$C_3H_4O_4$	104,06				1,20	2,83	5,69		
Jantaric	$C_4H_6O_4$	118,09				1,9	4,16	5,61		
Glutaric	$C_5H_8O_4$	132,12				1,06	4,31	5,41		
Adipic	$C_6H_{10}O_4$	146,14	(13℃) 40		(99℃) 10	2,1	4,43	5,41		
Citric	$C_6H_8O_6$		(20℃) <0,1			4,68	3,14	4,77	6,39	
Maleic	$C_4H_4O_4$	116,08				2,4	1,92	6,22		
Complexon 3	$C_{10}H_{14}N_2Na_2O_8 . 2H_2O$	372,24	(20℃) <0,1			10,7	1,99	2,67	6,16	10,3

It is seen that adipic acid, glutaric acid, and malonic acid have almost the same pK_{a2}, value, which may explain their similar buffering effect found by Frandsenem.[6]

Acids with lower value of pK_a should be less effective for the removal of sulphur dioxide.

3.4 Test gases

For the experiment of SO_2 absorption into the suspension were used gas mixtures. Three gas cylinders were used, each with different concentrations of sulphur dioxide, one with 3000 ppm of SO_2 (7% of oxygen and 13% of carbon dioxide, the balance is assured by nitrogen), other with 3170 ppm of SO_2 (7% of oxygen and 13% of carbon dioxide, the balance is assured by nitrogen) and the third with 3300 ppm of SO_2 (7% of oxygen and 13% of carbon dioxide, the balance is assured by nitrogen).

3.5 Measuring limestone solubility in water

To obtain the first information about the effect of organic acids on dissolving the limestone samples a few procedures were made. First the limestone samples were dissolved into distilled water for 24 hours at room temperature (18℃). Then to limestone suspension (with concentration of 20g.dm^{-3}) organic acids were added in two different concentrations (1 mmol.dm^{-3} and 4.3 mmol.dm^{-3}).[19,6,2]

After 24 hours the solutions were filtrated and calcium content of the solution (or calcium ion) was determined by atomic absorption spectrometry. The results are illustrated in Figure 29.

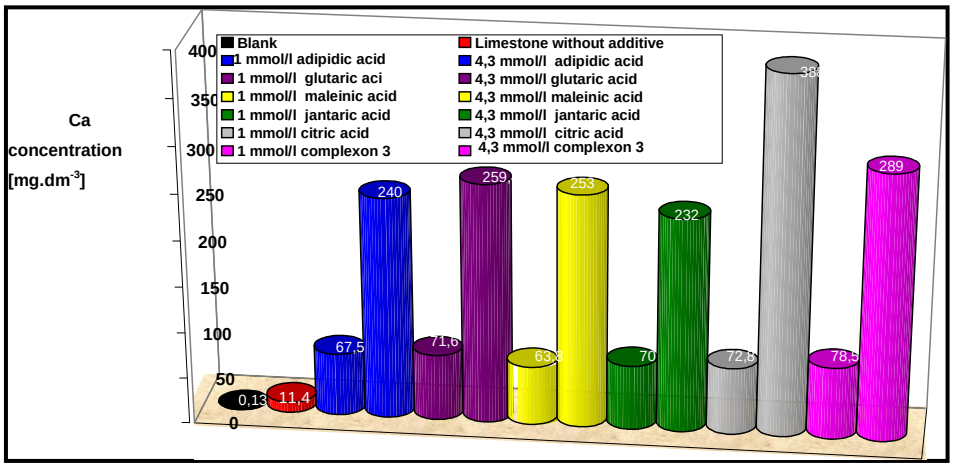

Figure 29 – Limestone solubility on water.

The figure 29 shows that the addition of acids substantially increases the concentration of calcium in the solution according to their concentration.

The dissolution of limestone was tested in distilled water. Afterwards, following the same process the effect of adding organic acids was tested. It was found that by adding organic acids the concentration of calcium ions in the suspension was increased several times. Dissolution of calcium carbonate increases by increasing organic acids concentration. For the dissolution of limestone a concentration of calcium in the solution of 11,4 mg.dm^{-3} was measured. After adding 1mmol.dm^{-3} of adipic acid a concentration of 67,5 mg.dm^{-3} of calcium was measured, and after increasing the concentration of adipic acid to 4,3 mmol.dm^{-3} the calcium concentration increased to 240 mg.dm^{-3}. The other tested acids had a similar effect. This confirms the assumption of positive impact of the addition of organic acids on the limestone dissolution.

3.6 Limestone dissolution in the presence of additives

To better understand the effect of additives on the release of calcium ions into the solution the dissolution of limestone slurry with sulphuric acid was measured. This measurement was carried out in laboratories TESO (Prague).

Dissolution of limestone can be determined by laboratory testing method Research-Cottrell (USA). In this method, the weight defined fraction of minced limestone (which is suspended in preheated distilled water) is titrated with sulphurous acid solution for maintaining a constant pH. [44]

For greater stability, this method has been modified and instead sulphurous acid sulphuric acid was used. Sulphuric acid reacts with calcium ions released into the solution for the creation of gypsum according reaction 47:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \qquad (47)$$

3.6.1 Device

The device consisted of thermostat bath filled with distilled water in which the sample was placed. Before the immersion, the suspension was stirred, the probe pH meter Fuel Standard 82 (Radiometer Copenhagen) was placed and on the thermo junction an automatic burette ABU 80 Auto burette was added (Radiometer Copenhagen). After starting the experiment sulphuric acid was added to the suspension from automatic burette and the pH was controlled by TTT 80 Titrator (Radiometer Copenhagen); the amount added was taken into account for maintaining constant pH. The sulphuric acid consumption signal was processed in the central pilot (Figure 30).

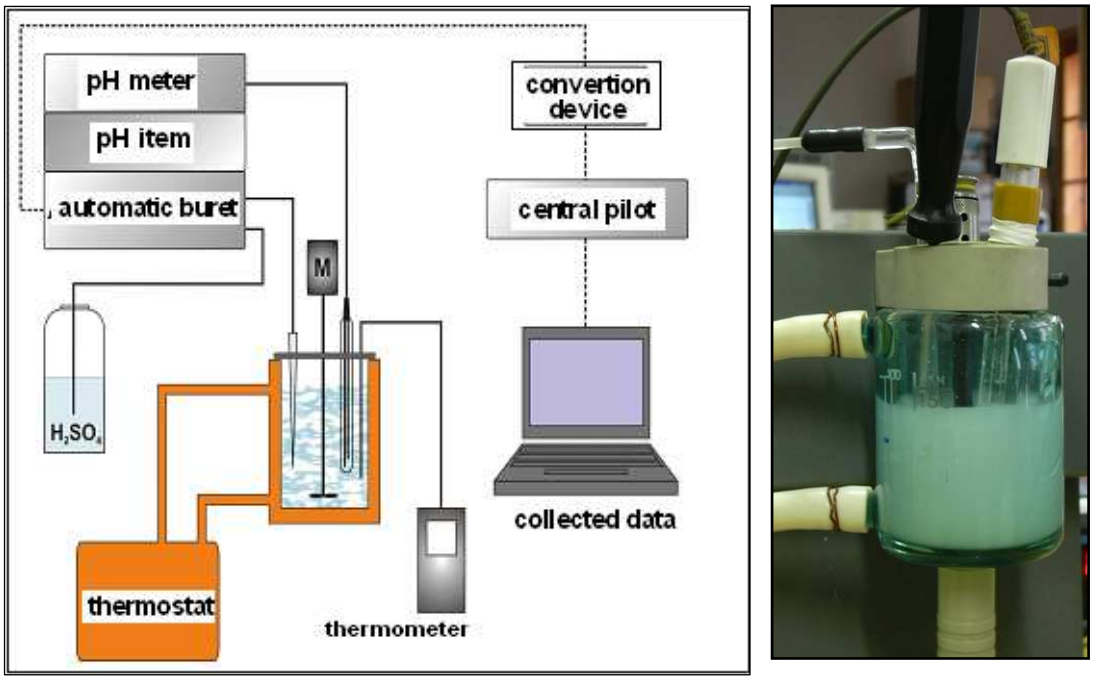

Figure 30 – Device diagram for measuring limestone dissociation.

3.6.2 Measurement procedures

The measurement was made with two samples, 1g of minced limestone ($CaCO_3$) mixed with 50 ml of distilled water. After preheating, the sample was placed inside a vessel with water (at 56ºC) and the starting pH was recorded. W ith an automatic burette, the exact quantities of sulphuric acid (with concentration of 0,4991 mol.dm^3) to the suspension, were dosed so that the pH was maintained at pre-set value (pH = 5). Titration was done stoichiometrically to react with limestone and dependence consumption of sulphuric acid was registered during the experiment time. Stoichimetrically, 1g (99%) $CaCO_3$ corresponds to 19,83 ml of sulphuric acid (with a concentration of 0,4991 mol.dm^{-3}). After adding organic acids to the suspension (always with the same concentration of 4,3 mmol.dm^{-3}) limestone dissolution was monitored according to the speed of change during titration.

3.6.3 Results and discussion

In this section it will be analysed and discussed the dissolution of limestone samples and forward conversion into calcium sulphate (gypsum) product from the reaction with sulphuric acid as function of time (according to equation 47).

Figure 31 shows the results of the comparison between natural limestone Certovy schody and pure $CaCO_3$. Limestone was significantly more reactive.

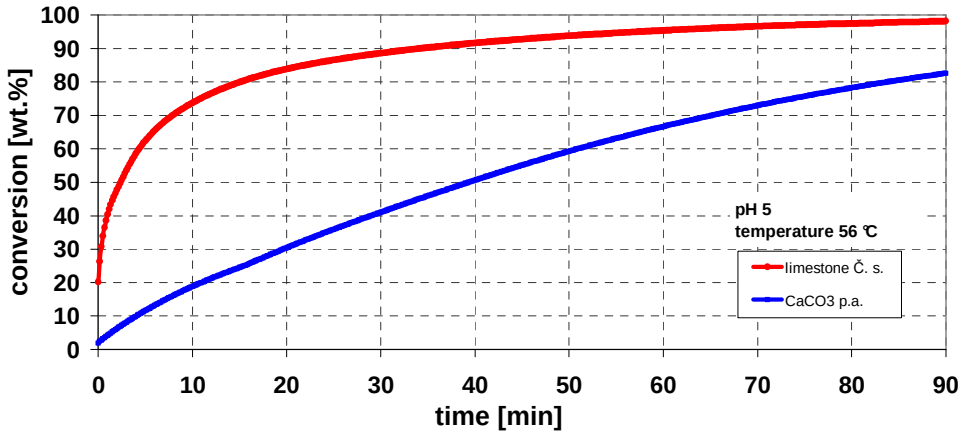

Figure 31 – Limestone conversion compared with $CaCO_3$.

The results of conversion of limestone and pure $CaCO_3$ with sulphuric acid under constant pH (=5) show that limestone is more reactive than pure calcium carbonate sample; after 20 minutes of measurement limestone had a conversion of 84% compared to the 30% of $CaCO_3$ These results show that smaller particles have a higher absorption capacity. Smaller particles have higher surface area; this increases the dissolution potential and the releasing of calcium ions into the solution. This process depends mainly on the particles surface, and is supported by the BET method; limestone has a BET surface of 2,061 m^2.g, and $CaCO_3$ of 0,063 m^2.g (Table 22).

Temperature does not influence limestone conversion (Figure 32).

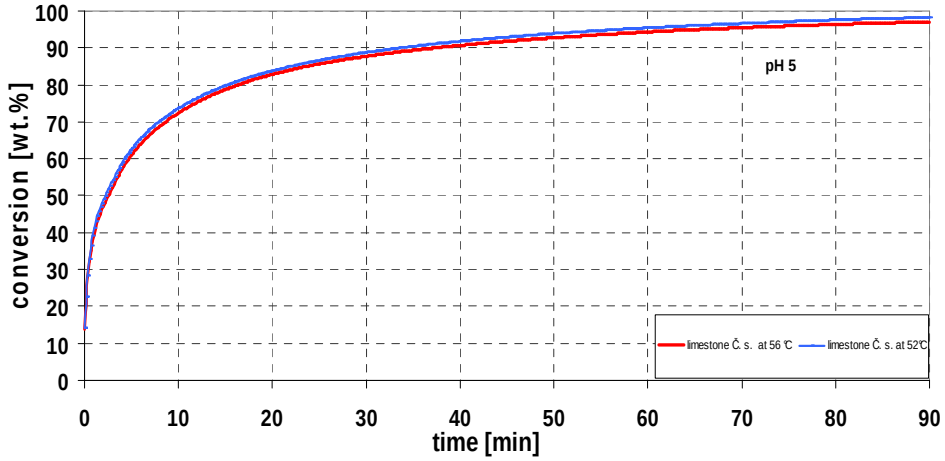

Figure 32 – The influence of temperature on limestone conversion.

Measurements of limestone and pure $CaCO_3$ conversion with sulphuric acid at constant pH (=5) were made with different temperatures, respectively 52ºC and 56ºC, showing very small differences between them; however at 52ºC limestone had a faster conversion. Because the equilibrium on the dissociation process is shifted, pH increases when the temperature increases.

For experimental test the temperature of 56ºC was chosen (it is used on the power plants).

Positive influence of dicarboxylic acids is shown in Figure 33.

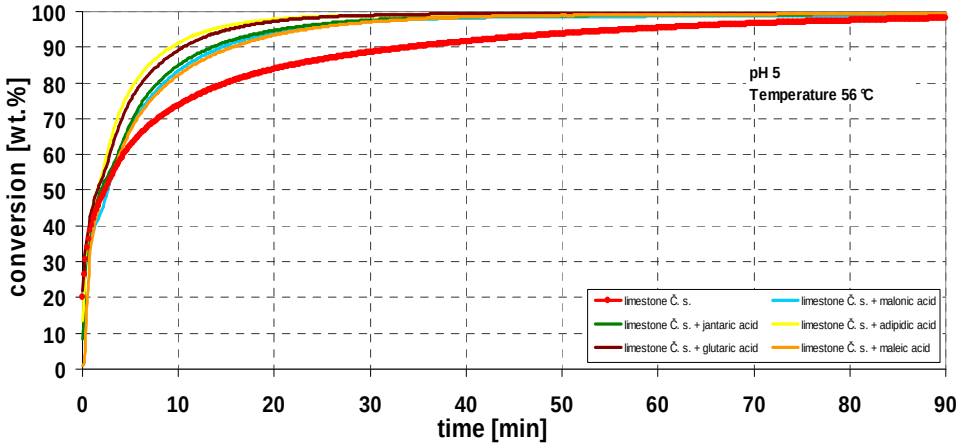

Figure 33 – Influence of addition of dicarboxylic acids on limestone conversion.

When of the dissolution test (and forward conversion to sulphates) with sulphuric acid at constant pH (=5) 91% a conversion of limestone with adipic acid, after 10 min of measurement, against 74% with no additive.

The test done with glutaric acid had almost the same result as with adipic acid, the conversion increased from 74% (without additive) to 89% with the addition of 4,3 mmol.l^{-1}.

Jantaric acid had positive effect but not as positive as adipic or glutaric acid. The addition of jantaric acid to the limestone suspension increased the conversion from 74% to 85%. The value of jantaric acid pk_{a1} is lower the one from adipic or glutaric acid, which can explain the differences in the effect. in the dissolution process.

With the use of malonic acid as additive, after 10 minutes of measurement the conversion of limestone increased from 74% to 83%.

Maleic acid used on the test of limestone conversion with sulphuric acid, shows a similar effect to the one in which malonic acid was used. Conversion increases after 10 min of experiment from 74% to 83% in result of adding maleic acid.

Organic acids can also influence negatively the limestone conversion, such as citric acid and oxalic acid (Figure 34).

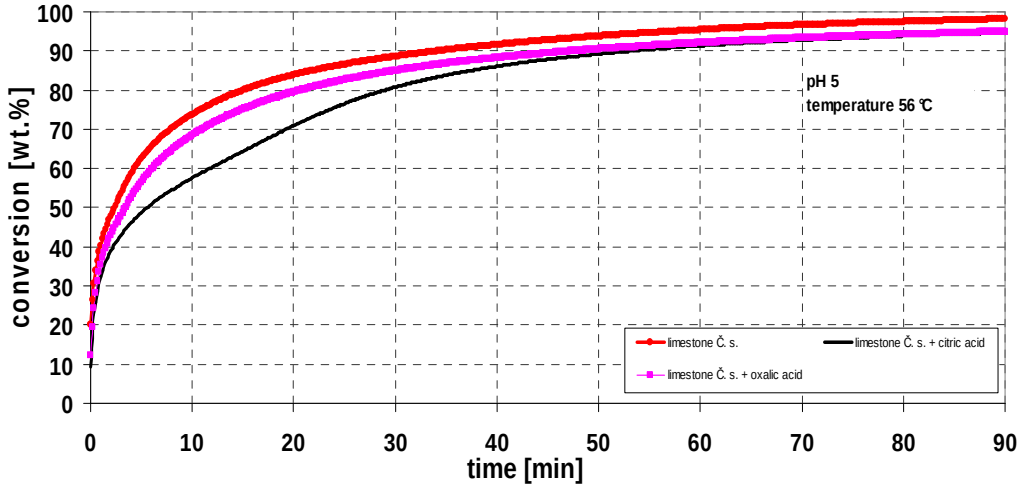

Figure 34 – Influence of the addition of citric and oxalic acid on limestone conversion.

During the test of influence of citric acid on the limestone suspension with sulphuric acid (under constant pH) negative effects were observed on the limestone conversion. The conversion of limestone after 10 minutes of measurement decreased from 74% to 57%.

Citric acid can block the porous surface of limestone forming complexes, thus avoiding the SO_2 penetration on the solid sorbent.

Oxalic acid had not such a negative impact as citric acid. With the addition of oxalic acid the conversion of limestone decreased from 74% to 71%. Once again the effect of these two additives can be explained by their low value of the pk_{a1}.

Figure 35 shows the positive effect of maleic and adipic acid addition on pure $CaCO_3$ suspension. It is seen that the influence on the conversion process is higher than the one observed with limestone.

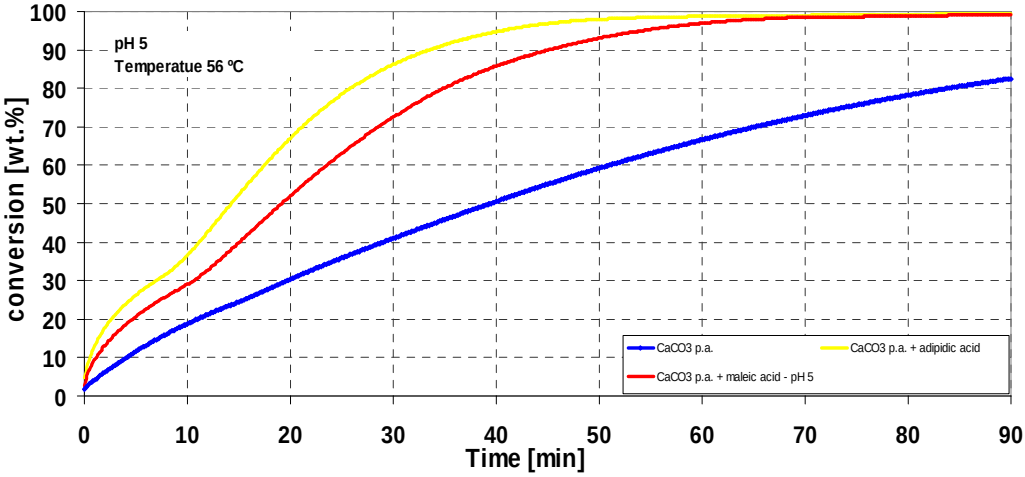

Figure 35 – Influence of the addition of maleic and adipic acid on pure $CaCO_3$.

The addition of adipic acid to the pure $CaCO_3$ suspension, after 30 minutes of measurement increased the conversion from 42% (without additive) to 87%. Maleic acid has a similar effect but not so good; comparing the two conversions, by adding this acid, the conversion increased from 42% to 73%. These differences are explained by the values of pk_{a1}, adipc acid has higher pk_{a1} value than the one of maleic acid.

Figure 36 shows that the conversion of pure $CaCO_3$, decreases by increasing the pH.

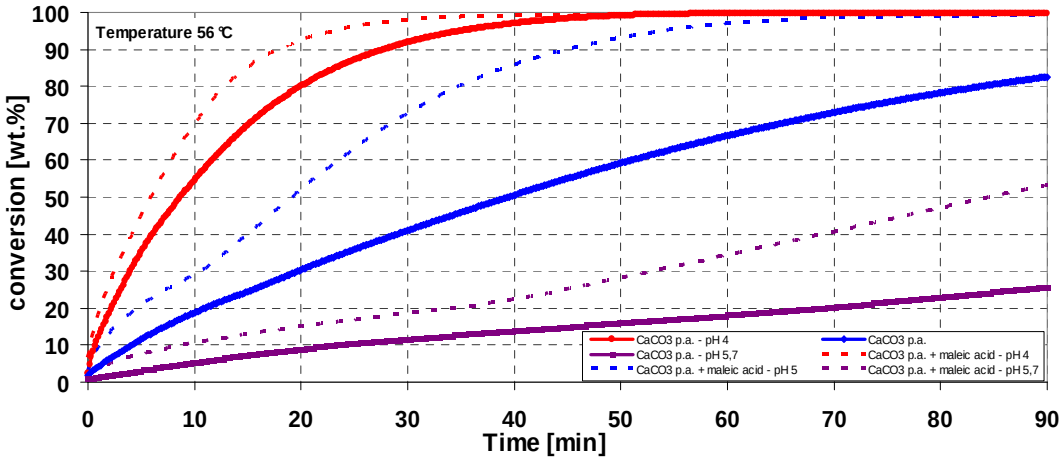

Figure 36 – Pure $CaCO_3$ conversion with and without maleic acid at different pH.

In figure 36 is shown the effect of pH on pure $CaCO_3$ suspension. The measurements were carried at pH 4, 4,5, and 5,7 and the conversions of calcium carbonate, after 20 minutes were 80%, 30% and 9% respectively.

Adding hydrogen ions (helping the reduction of calcium carbonate group) has an active role on the dissolution - at lower pH the dissolution is faster.

3.7 SO_2 absorption in limestone slurry

In the selection of experimental devices, the possibility of using a continuous stationary reactor in steady-state was considered. For example, mass flow, composition of streams, temperature, pressure, density, viscosity, etc, are constant. The system would be very good, but also would require new device acquisition. For these reasons tests in laboratory-scale were carried out on selected non-continuous reactor (see Figure 37), in which the parameters streams are functions of time.

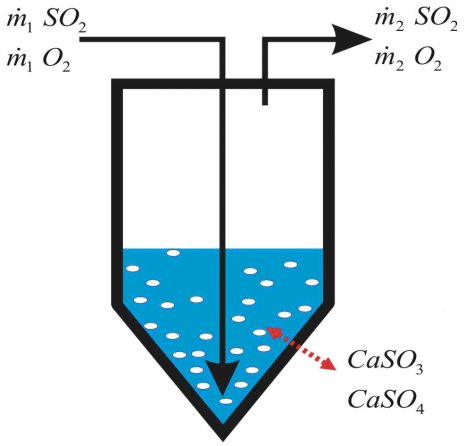

Figure 37 – A schematic diagram of sulphur dioxide absorber reactor.

The molar flow of SO_2 in the process can be seen as follows:

$$SO_2 input - reacted\ SO_2\ at\ stake = SO_2 output + accumulated\ SO_2$$

It is easy to express mathematically as follow:

$$\dot{V}^0 y_i^0 - V_r k x_i^{\ n} = \dot{V} y_i + V_r \frac{dx_i}{d\tau} \qquad (48)$$

$\dot{V}^0$ gas flow [$m^3.s^{-1}$] y_i^0 initial concentration of SO_2 [$mol.m^{-3}$]

k reaction rate constant y_i concentration of SO_2 in gas phase [$mol.m^{-3}$]

V_r reaction volume [m^3] x_i concentration of SO_2 in liquid phase [$mol.m^{-3}$]

T time [s]

3.8 Infrastructure

A scheme of the experimental installation is presented on the figure 38.

The gas mixture (containing SO_2) from the cylinder is divided in two flows. The first goes through a manostat, which serves to maintain a moderate pressure and in the case of high pressure this can be decreased by the use of cylinder valve, and the second flow of gas goes through a pipe (with a fine needle valve to regulate the flow) into the reactor. In the reactor the gas passes through the absorption suspension from the bottom to the top ensuring a good mixing of the solution (the bottom of the reactor is cone-shaped). The

entire reactor is immersed in the thermostat bath. The reactor is equipped with a pH probe meter that also measures temperature, which is submerged in absorption suspension. After passing through the absorption suspension the gas is cooled by a water cooler, returning the water to the reactor, and thus the dried gas (with dew point according to the temperature of the cooling water about 7 to 10℃) is held to the analyser (at working conditions with room temperature at 25℃ and 1 atm) and after through a gas meter in the exhaust hood. Before going into the analyser (Servomex Xentra 4900) it passes through a fridge, in order to condensate the reaming humidity on the gas, and to achieve a dew point below 1℃, because water vapour interferes with the absorbing band of SO_2.

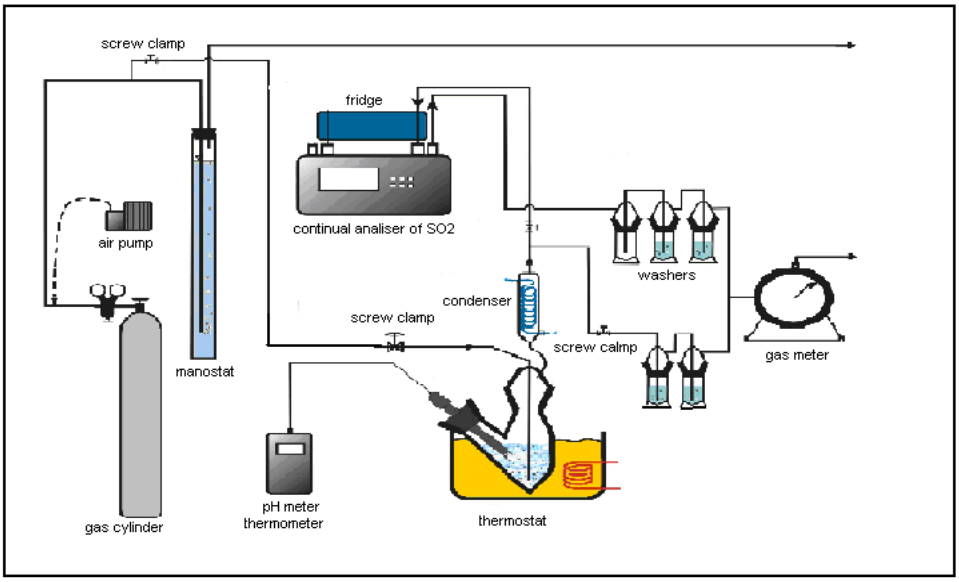

Figure 38 - Diagram apparatus to measure SO_2 absorption.

The volume of gas leaving the reactor and the analyser is measured using a wet gas meter. To protect the gas meter against acid corrosion by SO_2 two washers containing a solution of hydrogen peroxide were included.

Figure 39 presents the device used for the experiments. The cooling module and the analyser are located out of the hood due to space limitations.

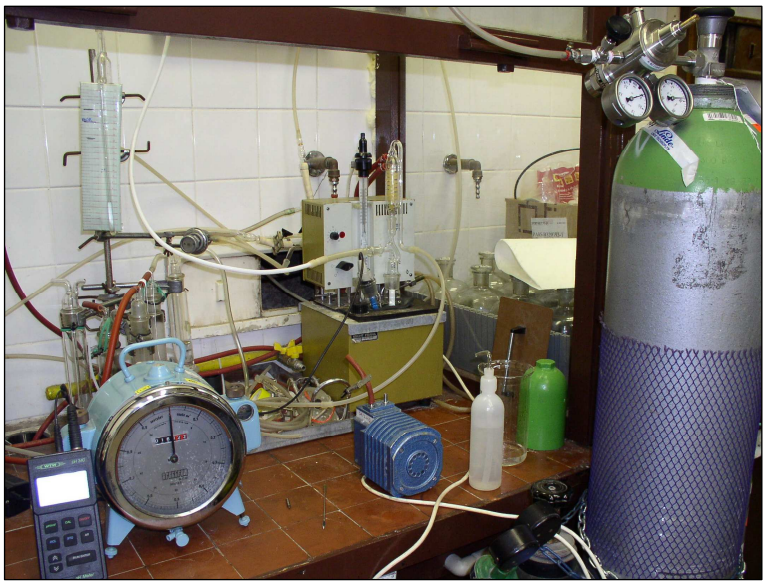

Figure 39 – Part of the apparatus located on the hood.

In Figure 40 the SO_2 analyser Servomex Xentra 4900 is presented.

Figure 40 – Servomax xentra 4900 analyser.

The reactor is made of glass (Figure 41) and was adapted with two ground joints, one for attaching glass extensions used for gas supply and drainage, and other for probe that measures the pH and temperature. The reactor was submerged in the thermostat bath. (Figure 39).

Figure 41 – Detail of the reactor.

In the upper part of the glass reactor an extension for water condenser was adapted, also attached by ground-glass joint (Figure 42).

Figure 42 – Detail of water condenser.

Figure 43 presents the reactor filled with limestone suspension. The bottom of the reactor does not show settling of particles from suspension, and therefore it can be considered a well-mixed suspension.

Figure 43 – Mixing suspension detail.

3.8.1 Experimental procedure

For each experiment, after setting up the device, the thermostat bath was set on at the desired value of 60ºC, the analyser was set on (hea ting takes about 1 h), both the fridge and the pH meter were set on and the cold water was left open into the water condenser. Two grams of sample (limestone or pure $CaCO_3$) were prepared in analytical weight. The additives used were also prepared in analytical weight (the necessary quantities were previously calculated) and put into the reactor. By including 100 ml of distilled water one suspension was created. Most additives have been added to the suspension with a concentration of 4,3 $mmol.dm^{-3}$. The reactor was then immersed in the thermostat bath. The test gas valve was opened to the system and the data acquisition was initiated.

Before each experiment it was necessary to clean up the system from the residual SO_2, by flushing it with atmospheric air. With the effort of reducing as much as possible sorption of SO_2 in the internal surface of the pipes materials as polyethylene and polyterafluorethylen (PTFE) were used. During the experiments the gas flow rate was set to 60 $dm^3.h^{-1}$ (for working conditions with room temperature at 25ºC and pressure at 1 atm) and within intervals of five minutes the output values of SO_2 concentration on the gas flow, pH, temperature and wet gas meter display were registered. The analyser was regularly calibrated with calibration gases from Linde (for the zero of the analyser was

used nitrogen gas, and for the span of the analyser was used sample gas with 3300ppm of SO_2).

3.8.2 Experimental results computing and discussion

Data obtained from the measurements was processed using Microsoft Excel. The data of the concentration of SO_2 in the gas in ppm by volume, measured on the analyser, have been converted into $mg.m^{-3,}$ using the state equation for ideal gas at room temperature 25℃ and 1 atm of pressure, according to the follow ing equation:

$$C_{SO_2\,[mg.m^{-3}]} = \frac{C_{SO_2\,[ppm]} \cdot M_{SO_2\,[g.mol^{-1}]}}{24{,}05} * 10^6, \text{ where} \qquad (49)$$

$C_{SO_2\,[mg.m^{-3}]}$ SO_2 concentration.

$C_{SO_2\,[ppm]}$ SO_2 concentration.

$M_{SO_2\,[g.mol^{-1}]}$ Molecular weight of SO_2.

From the measured volume of gas mixture fed into the reactor during each experiment, it was possible to know the cumulative inflow of sulphur dioxide, by multiplying it by the inlet sulphur dioxide concentration (in ppm). And by the use of ideal gases equation it is known that one mole of an ideal gas has the volume of 24,05 L (working conditions with temperature at 25ºC and at 1 atm of pressure); the SO_2 fed into the reactor multiplied by the inverse value of this factor gives us the inlet number of moles of sulphur dioxide. Then multiplying it by the sulphur dioxide molar mass it is possible to compute the inlet mass of SO_2 fed into the reactor. The results were evaluated in graphs. Graphs show the measured output concentrations of sulphur dioxide depending on the cumulative mass flow of SO_2 on the entering stream and also the pH suspension.

The numerical calculations were done for $200mg.m^{-3}$ and $400mg.m^{-3}$ of SO_2 outlet concentrations. Mathematical integration of the area under the curve gives us a total output mass of $SO_{2.}$ By knowing the inlet concentration of gas it is possible to get the inlet quantity of sulphur dioxide that entered in the system, therefore, it is possible to find the amount of sulphur dioxide that was absorbed by subtracting the output mass of SO_2 to the inlet SO_2 mass (see Figure 44).

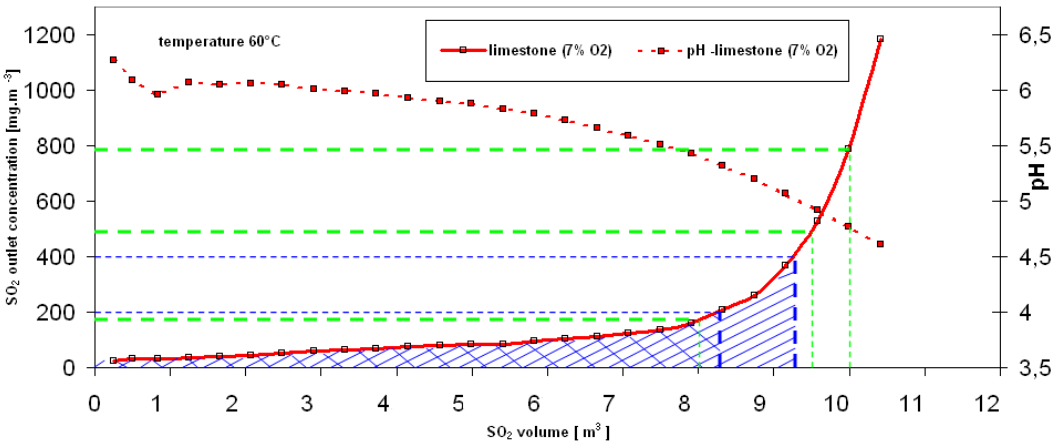

Figure 44 - Example of measured data.

The quantity of the reacted $CaCO_3$ (based on the stoichiometry of the reaction- multiplying the absorbed mass of SO_2 by the ratio between calcium carbonate and sulphur dioxide molar mass) and the conversion of the carbonate group were calculated for the outlet concentration of SO_2 of 200 $mg.m^{-3}$ and 400 $mg.m^{-3}$, respectively.

It was also calculated the desulphurization efficiency using the equation:

$$\eta_{des} = \frac{C_0 - C_1}{C_0}.100 \text{ , where} \qquad (50)$$

η_{des} Is the sulphur dioxide removal efficiency [%]

C_0 input concentration [$mg.m^{-3}$]

C_1 output concentration [$mg.m^{-3}$]

For the suspension of pure $CaCO_3$ the desulphurization efficiency was computed after being admitted 300 mg of sulphur dioxide into the reactor. And for the limestone suspension SO_2 removal efficiency was made for a cumulative mass of SO_2 (800 mg, 950 mg and 1000 mg) into the reactor.

To be able to evaluate the absorption of SO_2 by the system surfaces was carried out one measurement with an empty reactor. To evaluate the absorption capacity of water a measurement with a reactor filled with 100ml of distilled water (both measurements were made at 60 ºC) was made.

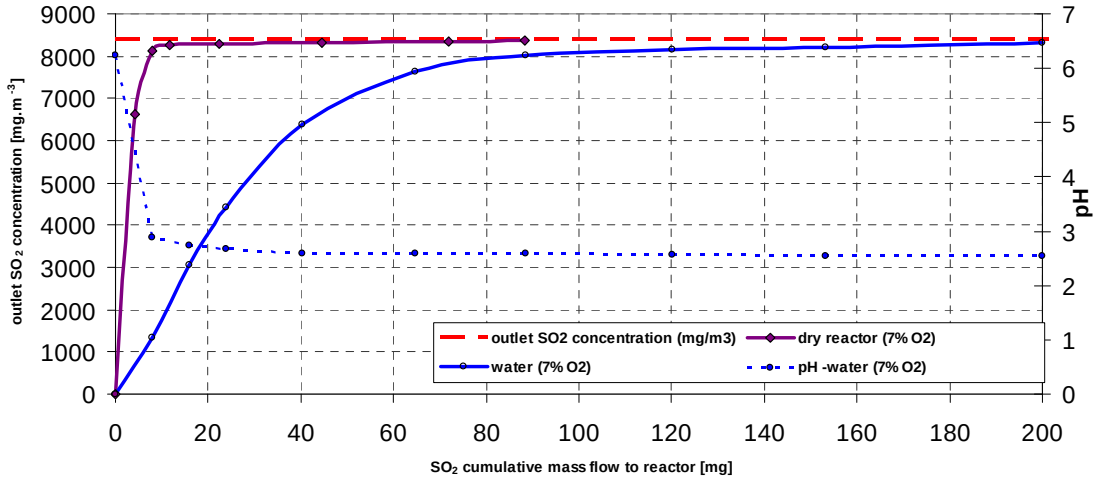

Figure 45 – Measurement with empty reactor and with blank.

Figure 45 shows the behavior of the experiment with the empty reactor, and it shows a rapid increase of SO_2 concentration in the reactor outlet gas (purple curve); this means that there is almost no absorption of SO_2 by the surfaces of the experimental system. The blue curve shows the SO_2 absorption by the distilled water, and it can be seen some absorption of SO_2 until the water gets saturated, followed by a rapid decrease in pH to a value around 2,6.

In the Figure 46 it is presented a comparison between the SO_2 absorption by distilled water and limestone suspension; it is observed a higher absorption capacity by limestone suspension.

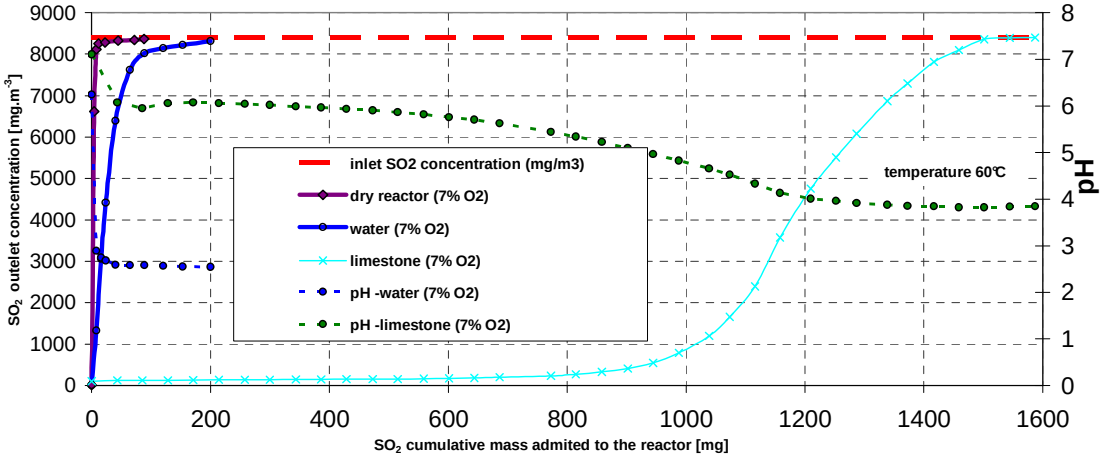

Figure 46 – Comparison between limestone and distilled water.

Table 25 – SO_2 absorption by distilled water.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen sample: distilled water (60℃)				
SO_2 cumulative mass admitted to the reactor [mg]	200	100	80	50
Absorbed SO_2 [mg]	32	30	29	25

In the calculations of the laboratory experiments carried out with limestone and pure $CaCO_3$ it has been always subtracted the value of SO_2 absorbed by the distilled water, an average value of 30 mg according experimental data on Table 25.

The Figure 47 shows the differences between absorption ability of limestone, pure $CaCO_3$ and pulverized pure $CaCO_3$. It is possible to observe that limestone is more reactive than pure $CaCO_3$ but less reactive than pulverized $CaCO_3$, due to the higher surface area of it. Table 26 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 27 presents the efficiency of SO_2 removal after admitting 300mg and 800 mg of SO_2 into the reactor.

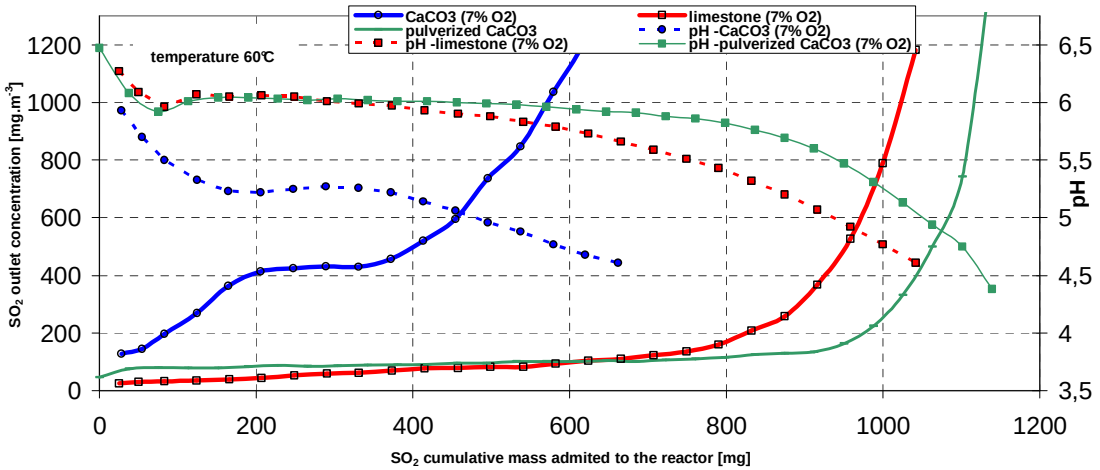

Figure 47 – Absorption ability of limestone, pure $CaCO_3$ and pulverized pure $CaCO_3$.

Table 26 – Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
To 200 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	54	84	4
Pulverized $CaCO_3$	908	1418	71
Limestone Čertovy schody	788	1231	63
To 400 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	160	250	13
Pulverized $CaCO_3$	973	1519	76
Limestone Čertovy schody	884	1381	71

Table 27 – Desulphurization efficiency for limestone and the two samples of $CaCO_3$ (pure and pulverized).

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen		
Sample	**Desulphurization efficiency [%]**	
	300 mg SO_2	**800 mg SO_2**
$CaCO_3$	95,1	73,8
Pulverized $CaCO_3$	99,0	98,0
Čertovy schody limestone	99,3	98,0

Until reaching the output concentration of 200 mg.m^{-3}, it is observed that:

I. limestone Čertovy schody absorbed 788 mg of SO_2, which represents a conversion of 63%;
II. in the case of pure $CaCO_3$ only 54 mg of SO_2 were absorbed (4% of conversion);
III. pulverized $CaCO_3$ reacted with 908 mg of SO_2 representing a conversion of 71%.

A similar effect was observed for 400 mg.m^{-3} of sulphur dioxide on the outlet concentration.

IV. limestone absorbed 884 mg of SO_2 (with 71% of converted calcium carbonate);
V. in the case of pure $CaCO_3$ were absorbed 160 mg of SO_2 (13% of conversion);
VI. in the case of pulverized limestone were absorbed 973 mg of SO_2 (76% of conversion).

Desulphurization efficiency was calculated for 800 mg of SO_2 on the cumulative entering stream. As expected, $CaCO_3$ had the lowest efficiency (73,8%) and pulverized $CaCO_3$ had the highest (98,6%), limestone had a desulphurization efficiency close to pulverized $CaCO_3$ (98%). These differences can be explained by the particles size, limestone and pulverized pure $CaCO_3$ samples have the smallest particles sizes and pure $CaCO_3$ have

the biggest particle size, smaller particles have higher surface area available for the absorption reaction of SO_2 (see tables 20 and 21).

Figure 48 presents the influence of glutaric acid added in different concentrations to the suspension of pure $CaCO_3$. It is observed a positive influence with the increasing of acid concentration. It can be seen that the pH is changing according to the desired interval of the values for the process.

Table 28 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. In the Table 29 is presented the efficiency of SO_2 removal after admitting 300mg of SO_2 into the reactor.

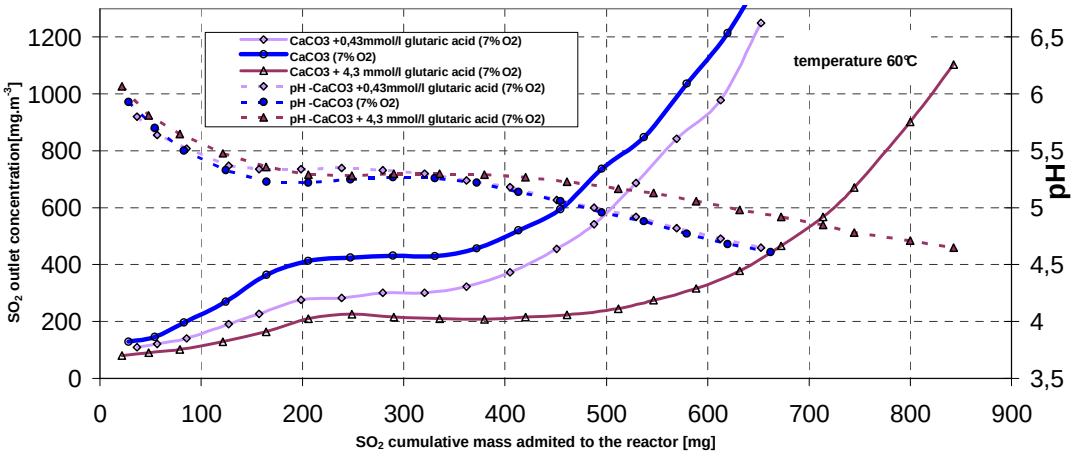

Figure 48 – Influence of glutaric acid on absorption of SO_2 by pure $CaCO_3$ suspension.

Table 28 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	54	84	4
$CaCO_3$ + 0,43 mmol/l glutaric acid	103	161	8
$CaCO_3$ + 4,3 mmol/l glutaric acid	174	272	14
to 400 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	160	250	13
$CaCO_3$ + 0,43 mmol/l glutaric acid	378	591	30
$CaCO_3$ + 4,3 mmol/l glutaric acid	607	948	48

Table 29 - Desulphurization efficiency of $CaCO_3$ suspension with glutaric acid.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen	
Sample	**Desulphurization efficiency [%]**
	To 300 mg SO_2
$CaCO_3$ p.a.	95,1
$CaCO_3$ p.a. + 0,43 mmol/l glutaric acid	96,6
$CaCO_3$ p.a. + 4,3 mmol/l glutaric acid	97,5

For pure $CaCO_3$ suspension with glutaric acid were tested two concentrations of 0,43 $mmol.dm^{-3}$ and 4,3 $mmol.dm^{-3}$.

In the case of 0.43 $mmol.dm^{-3}$ addition, until the output SO_2 concentration of 200 $mg.m^{-3}$, the absorbed quantity of SO_2 increased from 54 mg to (with 4% converted carbonate group) to 103 mg (with 8% $CaCO_3$ converted), and with the concentration of 4,3$mmol.dm^{-3}$ the amount of SO_2 absorbed increase to 174 mg of absorbed SO_2 (with 14% of converted calcium carbonate). Similarly, for 400 $mg.m^{-3}$ of SO_2 output concentration, with 0.43 $mmol.dm^{-3}$ of additive the absorbed SO_2 amount increases from 160 mg (with 13% converted $CaCO_3$) to 378 mg (30% of conversion) and with the concentration of 4.3 $mmol.dm^{-3}$ the absorbed quantity increases to 607 mg of SO_2 (with 48% of converted $CaCO_3$).

The desulphurization efficiency, until 300mg of SO_2 fed to the reactor, increases from 95,1% to 96,6% by adding 0,43 $mmol.dm^{-3}$of glutaric acid, and by adding 4,3 $mmol.dm^{-3}$ it reaches the value of 97,5%. In the experiments with glutaric acid addition, significant changes on pH were not observed compared with the experiments done with the suspensions without the use of additives. It can be concluded that increasing additive concentration increases sulphur dioxide absorption.

Figure 49 shows the influence of adipic acid added in different concentrations to the raw $CaCO_3$ suspension. As a similar effect to glutaric acid, the absorption capacity of the suspension increases with the increasing of acid concentration. The pH also changes within the desired value range for the process.

Table 30 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 31 shows the efficiency of SO_2 removal after admitting 300mg of SO_2 into the reactor

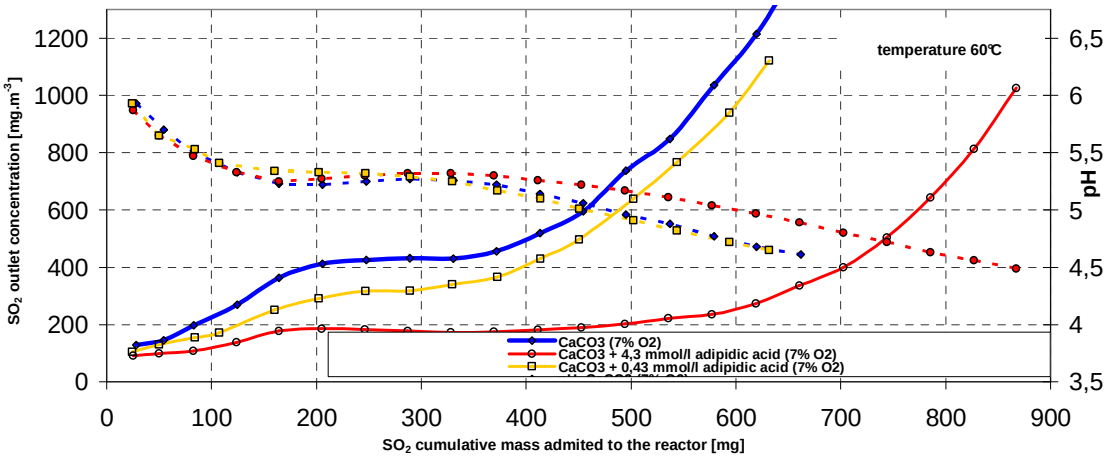

Figure 49 – Influence of the addition of adipic acid to $CaCO_3$ suspension.

Table 30 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen			
Sample	**Absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	54	84	4
$CaCO_3$ + 0,43 mmol/l adipic acid	94	148	7
$CaCO_3$ + 4,3 mmol/l adipic acid	450	703	35
to 400 mg.m^{-3} SO_2 outlet concentration			
$CaCO_3$	160	250	13
$CaCO_3$ + 0,43 mmol/l adipic acid	353	551	28
$CaCO_3$ + 4,3 mmol/l adipic acid	657	1027	52

Table 31 – Desulphurization efficiency with the addition of adipic acid.

Test gas: 3300 ppm SO_2, 7 % O_2, 13 % CO_2, Nitrogen	
Sample	**Desulphurization efficiency [%]**
	to 300 mg SO_2
$CaCO_3$ p.a.	95,1
$CaCO_3$ p.a. + 0,43 mmol/l adipic acid	96,3
$CaCO_3$ p.a. + 4,3 mmol/l adipic acid	98,0

In the experiment with pure $CaCO_3$ suspension with adipic acid were tested two concentrations: 0,43 mmol.dm^{-3} and 4,3 mmol.dm^{-3}. In the case of using 0,43 mmol.dm^{-3}, until reaching the output concentration of 200 mg.m^{-3} the absorbed quantity of SO_2 increased from 54mg (with a calcium carbonate conversion of 4%) to 94mg (7%

carbonate conversion). In the case of using 4,3 mmol.dm^{-3} it reached a value of 450 mg of absorbed SO_2 (with a carbonate conversion of 35%). Similarly, until it reached the outlet concentration of 400 mg.dm^{-3}, with 0,43 mmol.dm^{-3} the absorbed amount of SO_2 increased from 160 mg (13% $CaCO_3$ conversion) to 353 mg (28% calcium carbonate conversion). In the case of using 4,3 mmol.dm^{-3}, the sulphur dioxide absorbed amount increased to 657 mg (52% of carbonate conversion).

By adding 0,43 mmol.dm^{-3} of adipic acid the desulphurization efficiency at a cumulative quantity of SO_2 (300 mg) admitted into the reactor increased from 95,1% to 96,3%. By adding 4,3 mmol.dm^{-3} a desulphurization efficiency of 98% was reached.
Most of the experiments with adipic acid were done with $CaCO_3$ suspension, which was not very reactive itself. The use of additives can minimize the consumption of natural limestone.

Figure 50 shows the impact of the citric and oxalic acid on the absorption ability of limestone suspension. Both of these acids have a negative influence on the absorption ability, particularly citric acid in which the pH drops sharply. Table 32 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 33 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 into the reactor.

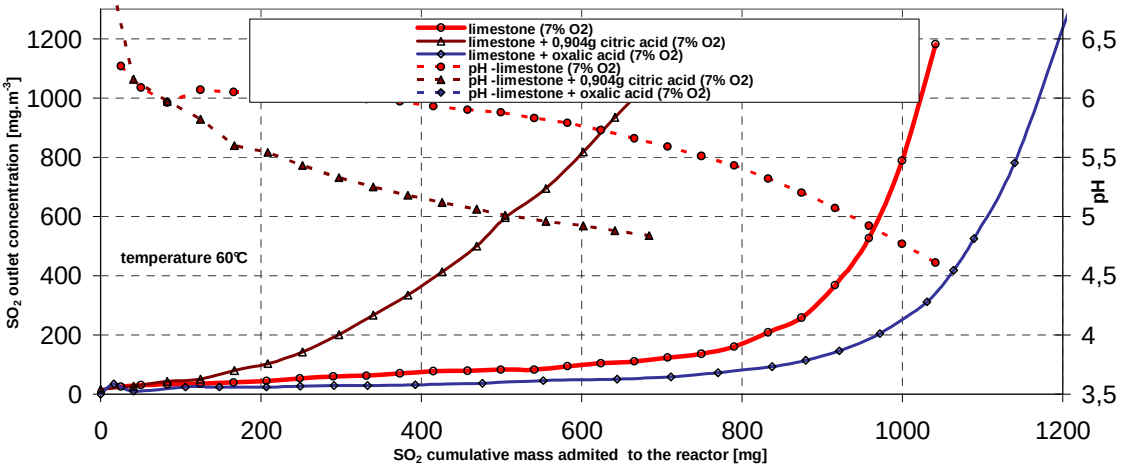

Figure 50 – Influence of the addition of citric and oxalic acid to limestone suspension.

Table 32 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas:3170 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen			
Sample	**Absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone+ 4,3 mmol/l citric acid	263	411	21
Limestone + 4,3 mmol/l oxalic acid	777	1214	62
Limestone	788	1231	63
to 400 mg.m^{-3} SO_2 outlet concentration			
Limestone + 4,3 mmol/l citric acid	380	594	30
Limestone + 4,3 mmol/l oxalic acid	851	1329	68
Limestone	884	1381	71

Table 33 – Desulphurization efficiency of absorption suspension with the addition of oxalic acid.

Sample	**Desulphurization efficiency[%]**		
	800 mg SO_2	**950 mg SO_2**	**1000 mg SO_2**
Limestone + 4,3 mmol/l citric acid	84,2	-	-
Limestone + 4,3 mmol/l oxalic acid	97,7	90,8	85,4
Limestone	98,0	94,4	91,0

During the experiments it was observed a negative influence of citric acid addition on the absorption of SO_2 by limestone suspension, the pH decreases rapidly to low values. Until reaching the output gas concentration of 200 mg.m^{-3} of SO_2, the quantity of absorbed sulphur dioxide decreased from 788 mg (with a $CaCO_3$ conversion of 63%) to 263 mg only (decreasing the conversion to 21%) in result of adding citric acid.

Similarly, until 400mg.m^{-3} of SO_2 in the gas output concentration, the SO_2 absorbed quantity decreased from 884 mg (with 71% of calcium carbonate conversion) to 380 mg (decreasing conversion to 30%) in result of adding citric acid. In the case of a cumulative mass fed into the system (800 mg of $SO_{2)}$, the desulphurization efficiency dropped from 98% to 84.2%.

The negative influence on absorbent abilities of scrubbing suspension due to organic acid addition (citric acid) is probably due to relatively high constant stability of the complex, which reaches values of 4.68 (log K, 25℃). As it c an be seen from measuring the impact of organic acids on the dissolution of limestone, citric acid was able to release more calcium into the solution, but while coupled to a form of a non-reactive species it does not react with SO_2 (or H_2SO_3). Another possible explanation is that citric acid can block the porous surface of limestone forming complexes, thus preventing SO_2 to penetrate in the solid absorbent structure.

Figure 51 presents the influence of jantaric and malonic acid on desulphurization ability of limestone suspension. Malonic acid had no effect on desulphurization, only pH decreased to low values compared to the ones of limestone suspension with no additive. Jantaric acid shows a positive effect, but only after the entering of a cumulative SO_2 mass flow in the reactor of around 850mg. Similarly, jantaric acid also reduced the pH of the suspension. Table 34 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 35 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

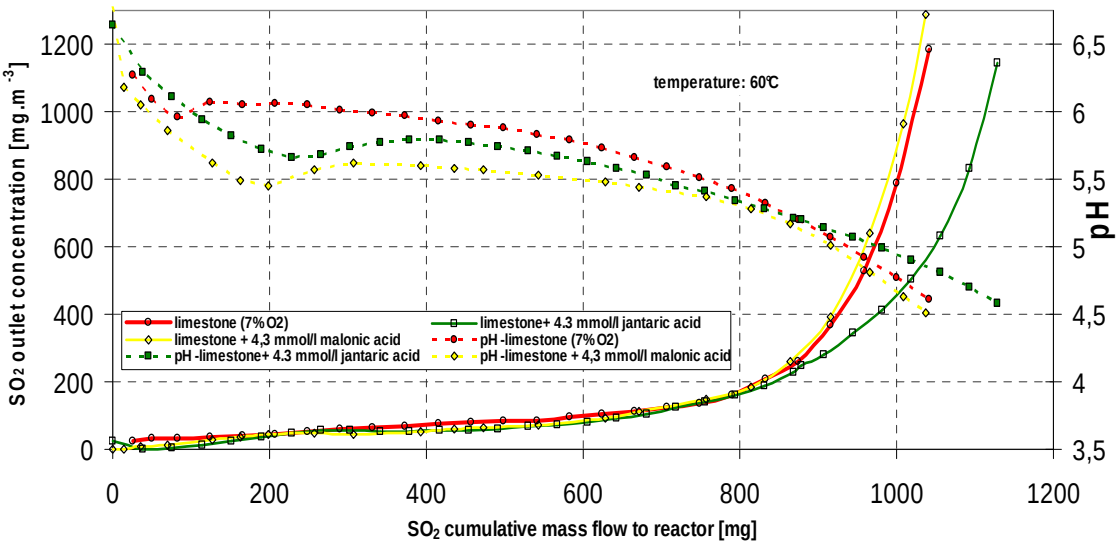

Figure 51 – Impact of malonic and jantaric acid to limestone suspension.

Table 34 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3170 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen			
Sample	**Absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 4,3 mmol/l jantaric acid	806	1259	64
Limestone + 4,3 mmol/l malonic acid	788	1231	63
to 400 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 4,3 mmol/l jantaric acid	934	1460	75
Limestone + 4,3 mmol/l malonic acid	876	1369	70

Table 35 – Desulphurization efficiency of limestone suspension with addition of jantaric and malonic acid.

Sample	Desulphurization efficiency [%]		
	800 mg SO_2	950 mg SO_2	1000 mg SO_2
Limestone	98,0	94,4	91,0
Limestone + 4,3 mmol/l jantaric acid	98,0	95,8	94,6
Limestone + 4,3 mmol/l malonic acid	97,8	92,9	88,7

In the desulphurization experiments with the gaseous mixture containing SO_2, jantaric acid had only a slightly positive effect on SO_2 absorbed by the limestone suspension in the final phase of the process.

By using this acid as an additive, until the output concentration of 200 $mg.m^{-3}$ of SO_2 was reached, the absorbed quantity of sulphur dioxide increased from 788 mg (with calcium carbonate conversion of 63%) to 806 mg (increasing the conversion to 64%). Similarly, to 400$mg.m^{-3}$ on the SO_2 output gas concentration the addition of jantaric acid increased the SO_2 absorption from 884 mg (with 71% of $CaCO_3$ conversion) to 934 mg (increasing the conversion to 75%).

The desulphurization efficiency, in the case of the cumulative entering amount of 1000mg of SO_2, was increased from 91% to 94,6% as a result of jantaric acid addition.

Initially the pH of the limestone suspension with jantaric acid addition dropped much faster than that of limestone suspension without organic acid addition, but it became greater than simple limestone suspension pH (on the point of 240 mg of entering amount of SO_2). It can be concluded that jantaric acid has a slow “start” but gradually it increases the desulphurization efficiency, as the cumulative amount of SO_2 fed into the reactor increases. At lower pH the limestone dissolution is higher and this makes possible to have more calcium ion in the suspension available to the absorption reaction of sulphur dioxide.

In the experiments regarding the influence of malonic acid on the limestone suspension conversion with sulphuric acid (under constant pH), have been observed similar positive effects to those of jantaric acid. With the use of malonic acid as additive after 10 minutes of experiment the conversion increased from 74% to 83%. Although in the SO_2 absorption experiments with limestone suspension, the addition of malonic acid did not have any effect until it reached the outlet SO_2 concentration of 200m $mg.m^{-3}$, and had a slightly negative effect until reaching the sulphur dioxide outlet concentration of 400 $mg.m^{-3}$. The quantity of absorbed sulphur dioxide decreased from 884 mg (with a conversion of 71%)

to 876 mg (decreasing the conversion to 70%). The desulphurization efficiency, in the case of the cumulative entering amount of 1000mg of SO_2, decreased from 91% to 88,7% as a result of malonic acid addition.

The behaviour of malonic acid remains unexplained. However, it is clear that is not a good candidate for additive on desulphurization processes.

Figure 52 shows that adipic and glutaric acids have a positive influence on SO_2 absorption by limestone suspension. In this case the pH of the suspension was slightly higher than the one observed in the suspension of limestone with no additives. Table 36 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 37 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

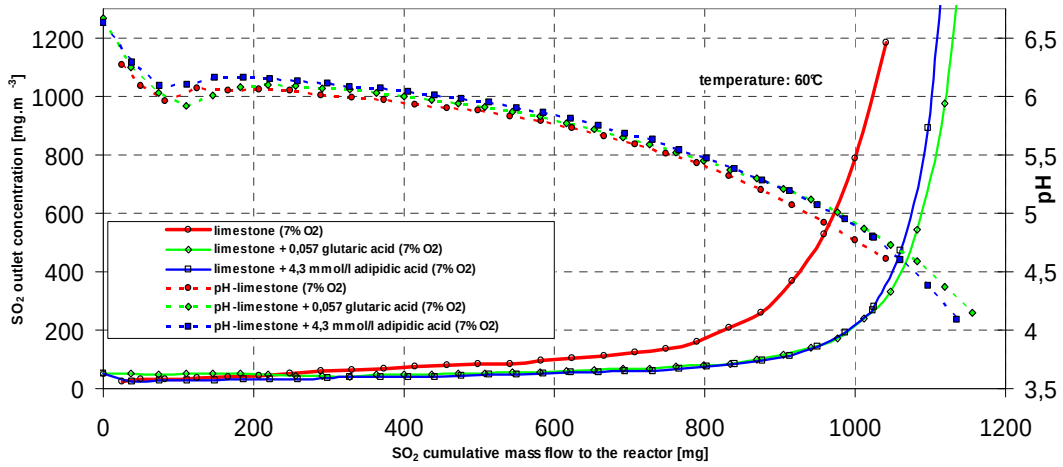

Figure 52 – Impact of adipic and glutaric acid on the limestone absorption capacity

Table 36 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas:3170 ppm SO_2, 7 % O_2, 13 % CO_2,nitrogen			
Sample	**Absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
To 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 4,3 mmol/l glutaric acid	953	1489	76
Limestone + 4,3 mmol/l adipic acid	955	1492	76
To 400 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 4,3 mmol/l glutaric acid	1018	1591	81
Limestone + 4,3 mmol/l adipic acid	1009	1576	81

Table 37 - Desulphurization efficiency of limestone suspension with the addition of glutaric and adipic acid.

Sample	Desulphurization efficiency [%]		
	800 mg SO_2	950 mg SO_2	1000 mg SO_2
Limestone	98,0	94,4	91,0
Limestone + 4,3 mmol/l glutaric acid	99,1	98,2	97,4
Limestone + 4,3 mmol/l adipic acid	99,1	98,3	97,4

The measurements with glutaric acid showed almost the same results as the ones done with adipic acid, and together they form the pair of the most tested additives in this work.

By adding 4,3 mmol.dm^{-3} of adipic acid to limestone suspension, until it reached the output concentration of 200 mg.$m^{-3,}$ the absorbed quantity of sulphur dioxide increased from 788 mg (with a conversion of 63%) to 955 mg (with a conversion of 76%), and by adding the same concentration of glutaric acid the absorbed amount of sulphur dioxide increased to 953 mg (also increasing the conversion to 76%).

Similar results were observed in the outlet concentration of 400mg.m^{-3}, in which limestone without additive absorbed 884 mg of SO_2 (with a conversion of 71%) and by adding 4,3 mmol.m^{-3} of adipic acid the absorbed quantity of sulphur dioxide increased to 1009 mg (with a conversion of 81%). By adding the same concentration of glutaric acid to the limestone suspension the absorbed amount of SO_2 increased to 1018 mg (with a conversion of 81%).

The SO_2 removal efficiency for both acids, used in similar concentrations (4,3 mmol.dm^{-3}), until the entering of 1000mg of SO_2 in the reactor, increased form 91% to 97,4%.

Figure 53 shows the influence of maleic acid on the desulphurization ability of limestone suspension. Until it reached a cumulative mass of 500mg in the reactor, the addition of maleic acid has a reduction effect on the absorption capacity; the pH falls rapidly. Then the situation reverses, and the pH in the suspension rises up again to a higher value than that of the limestone suspension without additive. Overall, as it can be seen in figure 53 this acid has a positive influence on the desulphurization ability. Table 38 presentes the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 39 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

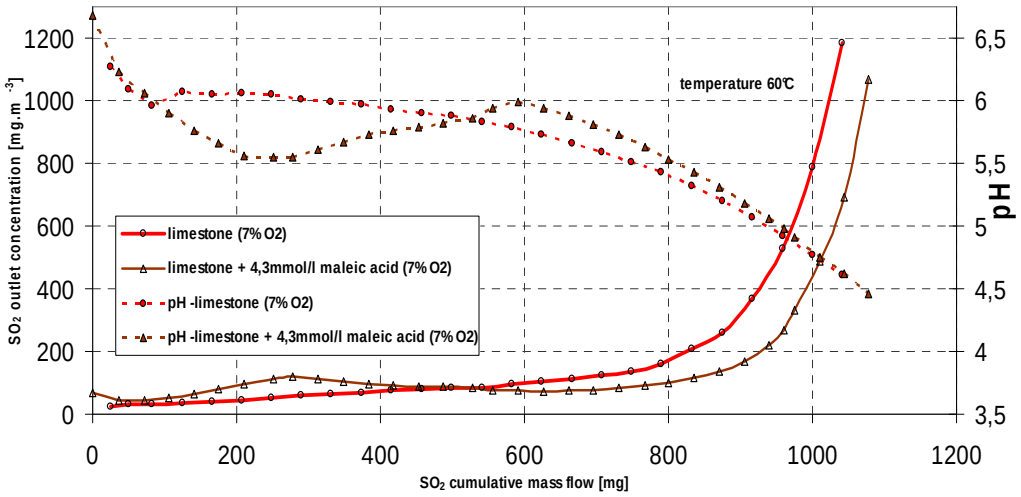

Figure 53 – Influence of maleic acid on absorption ability of limestone suspension.

Table 38 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas:3000 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 4,3 mmol/l maleic acid	886	1384	71
to 400 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 4,3 mmol/l maleic acid	948	1481	76

Table 39 - Desulphurization efficiency of limestone suspension with the use of maleic acid.

Sample	**Desulphurization efficiency [%]**		
	800 mg SO_2	**950 mg SO_2**	**1000 mg SO_2**
Limestone	98,0	94,4	91,0
Limestone + 4,3 mmol/l maleic acid	98,8	97,1	94,7

By adding maleic acid to the limestone suspension, in the first third of the experiment (around the value of 250 mg of cumulative mass of SO_2 fed into the reactor) the addition of this acid leads to a reduction on the efficiency of SO_2 removal, while a sharp fall on the pH is observed. But then it had a turn and the suspension with the additive became effective on SO_2 absorption, the pH of suspension increased to values greater than on that of limestone suspension without organic acid.

The absorbed quantities of SO_2 until the system reached the output concentration of sulphur dioxide of 200 $mg.m^{-3}$, increased from 788 mg (with a calcium carbonate conversion of 63%) to 886 mg (increasing the conversion to 71%) in result of maleic acid addition.

Similar situation happened for the output concentration of 400 mg. m^{-3} of SO_2, where the absorbed amount SO_2 increased from 884 mg (71% of $CaCO_3$ conversion) to 948 mg (increasing the conversion to 76%), in result of maleic acid addition. Desulphurization efficiency, for 950 mg of cumulative mass of SO_2 fed into the reactor, increased from 94,4% to 97,1% in result of maleic acid addition.

Figure 54 shows the influence of adding different concentrations of adipidic acid to the limestone suspension. Desulphurization efficiency increases by increasing the concentrations of additive. Table 40 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 41 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

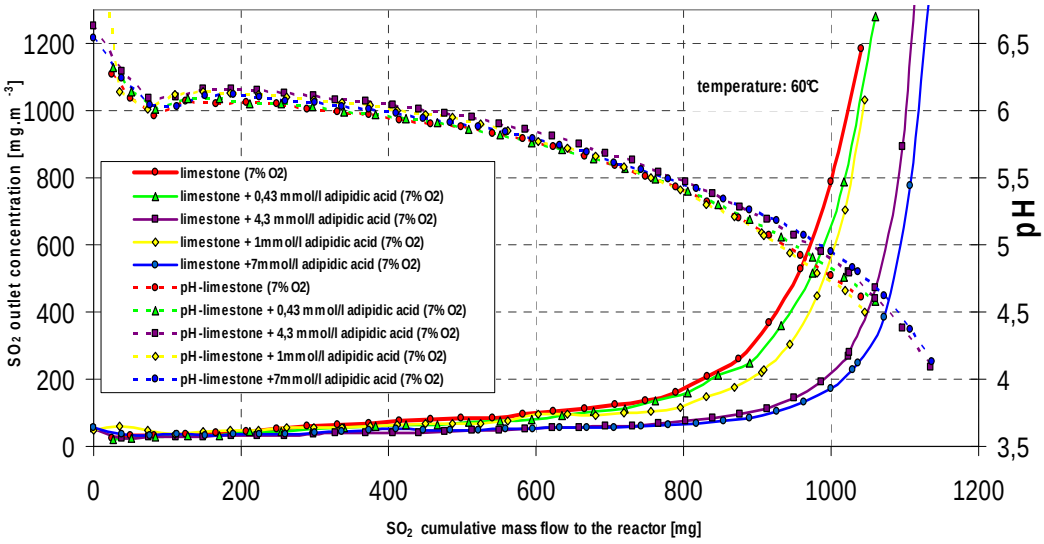

Figure 54- Influence of adipic acid on limestone suspension absorption.

Table 40 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3170 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 0,43 mmol/l adipic acid	802	1253	64
Limestone + 1 mmol/l adipic acid	852	1330	68
Limestone + 4,3 mmol/l adipic acid	955	1492	76
Limestone + 7 mmol/l adipic acid	979	1529	78
to 400 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 0,43 mmol/l adipic acid	903	1411	72
Limestone + 1 mmol/l adipic acid	928	1449	74
Limestone + 4,3 mmol/l adipic acid	1009	1576	81
Limestone + 7 mmol/l adipic acid	1034	1616	83

Table 41 - Desulphurization efficiency of limestone suspension with the use of adipic acid.

Sample	**Desulphurization efficiency [%]**		
	800 mg SO_2	**950 mg SO_2**	**1000 mg SO_2**
Limestone	98,0	94,4	91,0
Limestone + 0,43 mmol/l adipic acid	98,2	95,2	92,3
Llimestone + 1 mmol/l adipic acid	98,6	96,1	93,1
Limestone + 4,3 mmol/l adipic acid	99,1	98,3	97,4
Limestone + 7 mmol/l adipic acid	99,2	98,6	98,0

Increasing the concentration of the additive the desulphurization efficiency is improved. However, increasing concentrations above 7 mmol.dm^{-3} does not make sense, since the effect of 4,3 mmol.dm^{-3} to 7 mmol.dm^{-3} is quite close in terms of sulphur dioxide absorbed and in case of converted $CaCO_3$.

For real application is important high accuracy on the acid dosage.

Figure 55 shows the effect of complexon III addition to limestone Čertovy Schody suspension. It has a positive effect on the desulphurization ability. Although the pH during the first part of the measurement is lower than limestone suspension without additive, in the second part it became greater and afterwards the pH values of both suspensions were very similar. Table 42 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 43 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

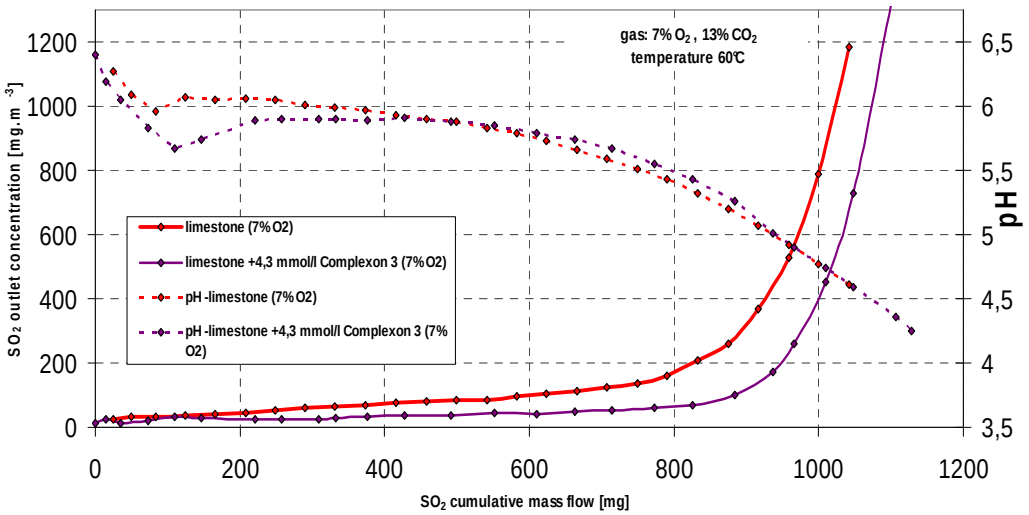

Figure 55 – Impact of complexon III on desulphurization ability of limestone suspension.

Table 42- Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas: 3000 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 4,3 mmol/l complexon III	910	1422	73
to 400 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 4,3 mmol/l complexon III	961	1501	77

Table 43 - Desulphurization efficiency of limestone suspension with the addition of complexon III.

Sample	**Desulphurization efficiency [%]**		
	800 mg SO_2	**950 mg SO_2**	**1000 mg SO_2**
Limestone	98,0	94,4	91,0
Limestone + 4,3 mmol/l complexon III	99,2	97,3	94,9

In the experiments of sulphur dioxide absorption, until the output SO_2 concentration of 200mg.m^{-3} was reached, the absorbed amount of SO_2 increased from 788 mg, for limestone suspension without additive, (with a conversion of $CaCO_3$ of 63%) to 910 mg (increasing the conversion to 73%) with this organic acid addition.

Similarly, until 400 mg.m^{-3} of SO_2 in the output concentration, the quantity of absorbed SO_2 increased from 884 mg (with 71% of converted $CaCO_3$) to 961 mg (increasing

conversion to 77%) in result of adding complexon III. Desulphurization efficiency, in the case of cumulative mass of SO_2 (950 mg) in the reactor, increased from 94,4% to 97,3% in result of the use of this additive.

The figure 56 shows the influence of monocarboxylic additives. All of them show a positive influence on absorption ability of SO_2 by limestone, but the best is acetic acid; formic acid keeps longer the pH at higher values. Table 44 presents the amount of SO_2 absorbed by the suspension, the amount of $CaCO_3$ that reacted with SO_2 to form $CaSO_4$ (calculated by stoichiometry of reaction) and its conversion. Table 45 shows the efficiency of SO_2 removal after admitting 800mg, 950mg, and 1000mg of SO_2 to the reactor.

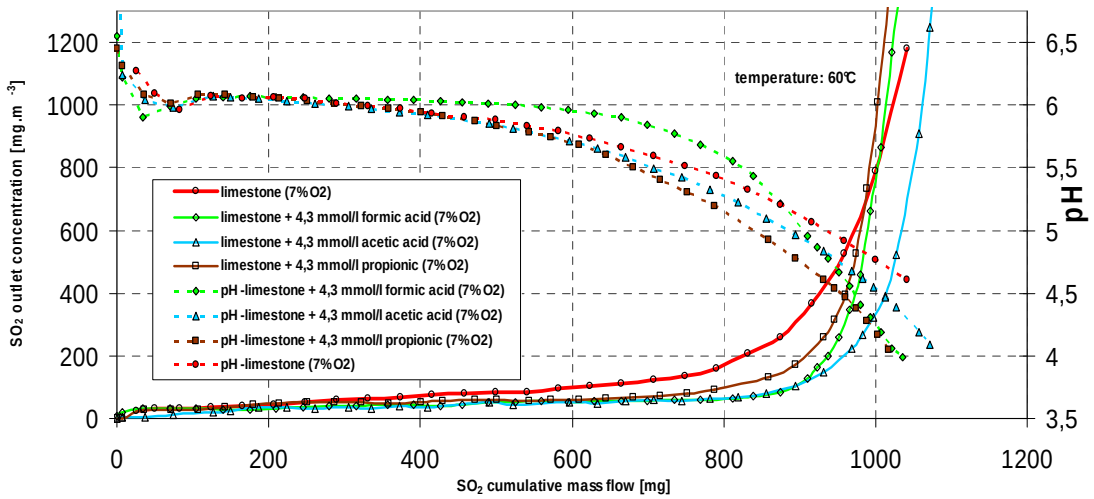

Figure 56 – Influence of acetic, formic and propionic acid on the absorption limestone suspension.

Table 44 - Absorbed sulphur dioxide mass, and the amount of $CaCO_3$ reacted and converted.

Test gas :3170 ppm SO_2, 7 % O_2, 13 % CO_2, nitrogen,			
Sample	**absorbed SO_2 [mg]**	**Quantity of reacted $CaCO_3$ [mg]**	**Converted $CaCO_3$ [%]**
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	788	1231	63
Limestone + 4,3 mmol/l formic acid	902	1409	72
Limestone + 4,3 mmol/l acetic acid	922	1440	74
Limestone + 4,3 mmol/l propionic acid	871	1360	70
to 200 mg.m^{-3} SO_2 outlet concentration			
Limestone	884	1381	71
Limestone + 4,3 mmol/l formic acid	936	1462	75
Limestone + 4,3 mmol/l acetic acid	976	1525	78
Limestone + 4,3 mmol/l propionic acid	922	1441	74

Table 45 - Desulphurization efficiency of limestone suspension with the addition of monocarboxylic acids.

Sample	Desulphurization efficiency [%]		
	800 mg SO_2	950 mg SO_2	1000 mg SO_2]
Limestone	98,0	94,4	91,0
Limestone + 4,3 mmol/l formic acid	99,2	97,0	91,0
Limestone + 4,3 mmol/l acetic acid	99,2	97,8	96,1
Limestone + 4,3 mmol/l propionic acid	98,8	96,0	88,6

The absorbed quantity of SO_2, until the output gas concentration of 200 mg.m^{-3} of sulphur dioxide is reached, increased from 788 mg (with a $CaCO_3$ conversion of 63%) to 902 mg (increasing the conversion to 72%) as result of formic acid addition. Similarly, until the output gas concentration of 400 mg. m^{-3} of SO_2 is reached, the amount of absorbed SO_2 increased from 884 mg (with a calcium carbonate conversion of 71%) to 936 mg (increasing the conversion to (75%) as result of formic acid addition.

The desulphurization efficiency, for example, for a cumulative mass of sulphur dioxide (950 mg) fed into the reactor, was increased from 94,4% to 97% as a result of formic acid addition. In the experiment with formic acid the suspension maintained the pH higher than the one of limestone suspension without organic acids addition.

Formic acid showed a positive influence on sulphur dioxide removal, although was not as good as adipic. The question here, as for the other monocarboxylic acids is the volatility, which could cause a reduction on their concentration on the suspension, increasing the emissions of these compounds, and by the way are creating corrosion problems on the equipment.

The influence of acetic acid in the experiments of limestone dissolution with sulphuric acid under controlled pH was positive, comparable to the one of adipic and glutaric acid. In line with the results of limestone conversion with sulphuric acid at constant pH (=5) were the experiments of SO_2 absorption by the limestone suspension – it was observed a positive influence. The absorbed quantity of SO_2, until the output gas concentration of 200 mg.m^{-3} is reached, increased from 788 mg (with a $CaCO_3$ conversion of 63 %) to 922 mg (increasing the conversion to 74%) as result of acetic acid addition. Similarly, until 400 mg.m^{-3} of SO_2 in the output gas concentration, is obtained the amount of absorbed SO_2 increased from 884 mg (71% of converted calcium carbonate) to 976 mg (increasing conversion to 78%).

The desulphurization efficiency was also improved, in the case of a cumulative mass of SO_2 fed into the reactor (950 mg), increasing from 94,4% to 97,8%. The pH value during the experiment was kept higher than the one of limestone suspension without additives.

Acetic acid has shown to enhance the SO_2 absorption by limestone suspension, its effect was very good and was almost comparable to the one of the adipic acid. The question is, as with formic acid already mentioned the volatility of this acid.

The addition of propionic acid was positive for enhancing the SO_2 absorption capacity of the limestone suspension, but the effect was weaker than that of formic acid. Only in the final stage of the experiment was observed a positive influence, as well as with formic acid. The absorbed quantity of sulphur dioxide, until the output concentration of SO_2 of 200 $mg.m^{-3}$, increased from 788 mg (with $CaCO_3$ conversion of 63%) to 871 mg (increasing the conversion to 70%) in result of propionic acid addition. Similarly, until 400 $mg.m^{-3}$ of SO_2 on the output gas concentration is obtained, increased the amount absorbed sulphur dioxide from 884 mg (with a conversion of calcium carbonate of 71%) to 922 mg (increasing the conversion to 74%) as result of propionic acid addition. Desulphurization efficiency, for example in the case of a SO_2 cumulative mass fed into the reactor (950 mg), was increased from 94.4% to 96% as result of propionic acid addition.

4 Conclusions

This work deals with the process of testing appropriate additives for limestone suspension in desulphurization processes.

During the laboratory experiments organic acids were tested as additives. Their influence has been tested in two different suspensions, one made of natural limestone (Čertovy schody) and the other produced with synthetic pure $CaCO_3$. For better understanding the factors that influence the WFGD process, the limestone dissolution was measured in water with and without the use of additives (the dissolution of carbonate group in the water was monitorized). The chemical conversion of calcium carbonate to calcium sulphate with the use of sulphuric acid has also been measured (while pH was kept under constant value =5).

The most relevant conclusions are summarized below:

- Pulverized $CaCO_3$ has higher impact on desulphurization ability than $CaCO_3$. It can be concluded that smaller particles have higher reactivity (smaller particles means higher surface area for reaction) – greater potential for releasing calcium ions in the suspension.

- The addition of organic acids increases the calcium ions concentration in the suspension.

- pH influence can be noticed in the graphs of reactivity – when pH decreases the reactivity increases (increasing the calcium carbonate conversion).

- Amongst all the tested additives the most effective were adipic and glutaric acid. Jantaric acid also showed positive effects, however it was not nearly effective as the adipic, or the glutaric acid. Malonic acid did not increased the efficiency of the desulphurization process (this cannot be really explained).

- The monocarboxylic acids, namely formic, acetic and propionic acid had all a positive influence in the desulphurization efficiency. But the best results were achieved with acetic acid - which was almost comparable to adipic and glutaric acid. The problem is that their volatility could cause a reduction of their concentration on the scrubbing liquid.

Amongst other additives (tricarboxylic acids) it was tested complexon III which had a positive impact and citric acid which had the worst performance.

As for the tested acids it has become clear that increasing the additive concentration improves the absorption capacity. However, the increase of the additive concentration from 4,3 $mmol.dm^{-3}$ to 7 $mmol.dm^{-3}$ didn't show a significant influence in the desulphurization efficiency as it can be seen in the results of the test of limestone suspension with different concentrations of adipic acid.

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